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Preparation and Characterization of Tertiary Phosphine Carbonyl Ruthenium (0) Complexes

Joann C. Bady
Eastern Illinois University

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Preparation and Characterization of Tertiary Phosphine Carbonyl Ruthenium (0) Complexes.

(TITLE)

BY

Joann C. Bady

THESIS

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Abstract

Dichlorocarbonyltris(triphenylphosphine)ruthenium (II), $Ru(CO)(Cl)_2(Ph_3P)_3$, was prepared by modification of a procedure reported to yield the dimer, $(Ru(CO)(Cl)_2(Ph_3P)_2)_2$. Dissolution of $Ru(CO)(Cl)_2(Ph_3P)_3$ in acetonitrile resulted in loss of triphenylphosphine and dimer formation.

Metathesis of $Ru(CO)(Cl)_2(Ph_3P)_3$ in hexane with excess tertiary phosphine yielded complexes of the type $Ru(CO)(Cl)_2(R_2R'P)_3$ where $R_2R'P$ is Ph_2MeP or $PhMe_2P$. ^1H and ^{31}P nmr spectra of these materials showed that two phosphines are mutually trans and cis to the remaining phosphine ligand. This metathesis reaction could not be used with tertiary alkyl phosphine to prepare analogous compounds.

Potentiostatic reduction of $Ru(CO)(Cl)_2(Ph_3P)_3$ in acetonitrile with excess Ph_3P at a platinum cathode gave the zero valent complex, $Ru(CO)(CH_3CN)(Ph_3P)_3$, in high yield. This compound has also been synthesized by electrolysis of the dimer mentioned above. The enhanced solubility of $Ru(CO)(Cl)_2(Ph_3P)_3$ relative to the dimer results in shorter electrolysis times.

Attempts to metathesize $Ru(CO)(CH_3CN)(Ph_3P)_3$ with Ph_2MeP, $PhMe_2P$ or Et_3P in acetonitrile yielded only mixtures of compounds as intractable oils.

Polarographic and voltammetric studies of $Ru(CO)(Cl)_2(Ph_2MeP)_3$ and $Ru(CO)(Cl)_2(PhMe_2P)_3$ in acetonitrile indicates that these materials are reduced irreversibly with the uptake of two electrons. Two electroactive species are formed in acetonitrile solutions of

these compounds. These species arise from tertiary phosphine/ acetonitrile exchange. Mass transport of the electroactive species is controlled by both kinetics and diffusion.

Acknowledgements

I would like to thank Dr. Edward O. Sherman, Jr. for his guidance, encouragment and extraordinary patience in this endeavor. Much appreciation is given to the faculty and staff for all their help.

My sincerest gratitude is given to my mother, Mrs. Earline Bady, for her unfailing confidence and support.

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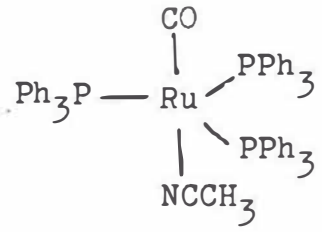
Introduction

Recent research in these laboratories has focused on the unusual chemical reactivity of ruthenium (0) complexes. One such complex is $Ru(CO)(CH_3CN)(P(C_6H_5)_3)_3$ synthesized by Olson (1). This compound was prepared electrolytically at a platinum cathode from a suspension of $(RuCl_2(CO)(P(C_6H_5)_3)_2)_2$ in acetonitrile which contained an excess of triphenylphosphine. The equations below illustrate the reduction process where triphenylphosphine is represented as Ph_3P:

$$Ru(CO)(Cl)_2(CH_3CN)(Ph_3P)_2 + 2e^- \longrightarrow Ru(CO)(CH_3CN)(Ph_3P)_2 + 2Cl^-$$

$$Ru(CO)(CH_3CN)(Ph_3P)_2 + Ph_3P \rightleftharpoons Ru(CO)(CH_3CN)(Ph_3P)_3$$

The product was characterized by its infrared spectrum which exhibited a weak nitrile stretching vibration at 2264 cm^{-1} and a strong band which is attributed to a carbonyl ligand at 1865 cm^{-1}. The ^1H nmr spectrum of the complex in toluene-d_8 gave a broad singlet centered at 7.1 ppm due to the phenyl protons and a sharp singlet at 0.71 ppm from the methyl protons of coordinated acetonitrile. The ratio of phenyl to methyl signals was 15:1 and an upfield hydride signal was absent. The ^{31}P nmr spectrum exhibited a sharp singlet at 51.88 ppm indicating that all phosphorous nuclei are in equivalent magnetic environments. On the basis of these spectroscopic data, the structure was assigned as trigonal bipyrimidal with the phosphine ligands in the equatorial positions:



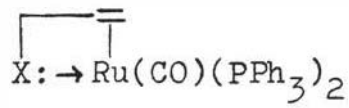
The complex, $Ru(CO)(CH_3CN)(PPh_3)_3$, has shown both traditional as well as unusual oxidative-addition behavior. In both cases, the metal complex inserts into an R-X bond. Rapid oxidative-addition reactions of methyl iodide, methylene chloride and benzyl chloride to $Ru(CO)(CH_3CN)(PPh_3)_3$ formed $RuI(CH_3)(CO)(CH_3CN)(Ph_3P)_2$, $RuCl_2(CO)(CH_3CN)(PPh_3)_2$ and $RuCl(\sigma\text{-}CH_2C_6H_5)(CO)(CH_3CN)(PPh_3)_2$, respectively. Such reactions of low valent metal complexes with these types of substrates are well known (2,3).

Unusual oxidative-addition behavior of $Ru(CO)(CH_3CN)(PPh_3)_3$ was observed with substituted allylic olefins such as allyl chloride, allyl acetate, allyl methyl ether, allyl thiourea and allyl thiocyanate. These substituted allylic olefins reacted with the zero valent compound to yield air stable organometallic products which analyzed as $RuX(\eta^3\text{-}C_3H_5)(CO)(PPh_3)_2$ where X = -Cl, $-OCOCH_3$, $-OCH_3$, -NCS or $-NHCSNH_2$. A general equation for this novel oxidative-addition reaction is shown below:

$$Ru(CO)(CH_3CN)(PPh_3)_3 + C_3H_5X \longrightarrow RuX(\eta^3\text{-}C_3H_5)(CO)(PPh_3)_2 + CH_3CN + PPh_3$$

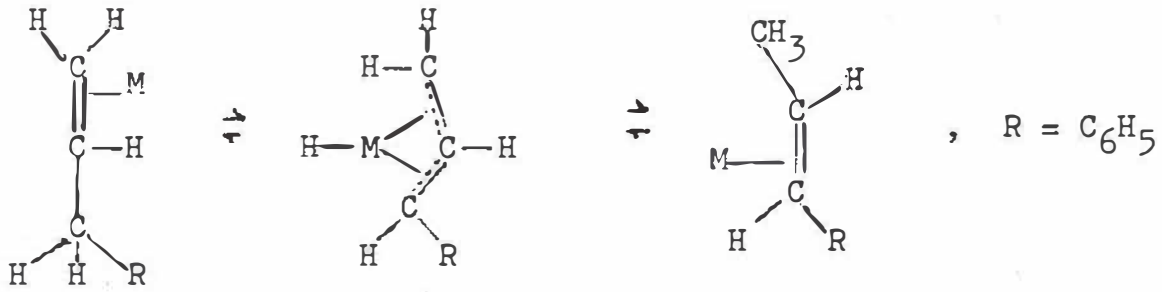
The allylic olefins which undergo this unusual oxidative-addition behavior contain, in each case, an allylic substituent which has one or more lone electron pairs on an atom of the substituent group. It has been proposed (1) that a coordinative interaction

of this nucleophilic substituent with the metal center,



maybe involved as a reaction intermediate and may make the oxidative-addition reaction easier.

$Ru(CO)(CH_3CN)(PPh_3)_3$ also has shown catalytic behavior in the isomerization of allylbenzene to β-methylstyrene. This reaction is thought to involve a 1,3-hydrogen shift from the allylic position to the double bond by way of an η^3-allyl hydride intermediate:



The formation of the hydride η^3-allyl intermediate is a special case of the oxidative-addition activity of substituted allylic olefins described above.

The principal object of this research was to synthesize a series of related ruthenium (0) species of the type $Ru(CO)(CH_3CN)(R_3P)_3$ where R_3P = $(C_6H_5)_2CH_3P$, $C_6H_5(CH_3)_2P$ and $(C_2H_5)_3P$. In this series, the donor strength of the ligand should produce an appreciable change in electron density at the metal center which should in turn affect both the oxidative-addition behavior and the isomerization activity of these ruthenium (0) compounds.

Two possible methods for the preparation of these new

ruthenium (O) compounds seemed feasible. Firstly, direct metathesis of $Ru(CO)(CH_3CN)(PPh_3)_3$ with the tertiary phosphine might lead to the desired products (4):

$$Ru(CO)(CH_3CN)(PPh_3)_3 + 3R_3P \xrightarrow{CH_3CN} Ru(CO)(CH_3CN)(R_3P)_3 + 3Ph_3P$$

$R_3P = (C_6H_5)_2CH_3P,\ C_6H_5(CH_3)_2P,\ (C_2H_5)_3P$

Alternatively, an electrochemical method similar to that devised by Olson (1) could be used. This latter method would require the initial synthesis of the ruthenium (II) compounds, $RuCl_2(CO)(R_3P)_3$, where $R_3P = (C_6H_5)_2CH_3P,\ C_6H_5(CH_3)_2P,\ (C_2H_5)_3P$. These substances would then be reduced potentiostatically to obtain the required ruthenium (O) complexes.

Experimental

1. General Methods

All of the syntheses and the handling of compounds were performed either under nitrogen with inert atmosphere techniques or under nitrogen in a Vacuum Atmosphere Dri-Lab glove box, Model HE 43/243, with Dri-train, Model HE 493. The glove box was checked daily for oxygen contamination with a 25 w% solution of diethyl zinc in toluene. If no fumes were present when the bottle was opened, then the glove box contained less than 5 ppm of oxygen.

Infrared spectra were recorded on a Perkin-Elmer grating spectrophotometer, Model 337. Solid state spectra (4000-400 cm^{-1}) were obtained from Nujol mulls between KBr plates. For all spectra, calibration was accomplished using the 1602 cm^{-1} and 907 cm^{-1} aborption bands of a polystyrene film.

The ^{31}P nmr spectra were obtained on a Varian XL-100 spectrometer at 100 MHz. An external reference of H_3PO_4 was employed for ^{31}P nmr spectra. ^{31}P nmr spectra were measured at the University of Illinois, Urbana, Illinois. ^{1}H nmr spectra were obtained on a Varian T-60 spectrometer at 60 MHz. An internal reference of TMS was used for some ^{1}H nmr spectra.

Polarograms and voltammograms were obtained with a Heath Module polarograph, model EUA-19-2. A Varian Associates x-y recorder, model F-80, was used to record the current-voltage curves.

Melting points were obtained using a Thomas-Hoover capillary melting point apparatus and the melting points were uncorrected.

Analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee. Only single analyses were obtained for each compound.

2. Materials

a) Phosphine Ligands

The following phosphines were obtained from E. O. Sherman and had been prepared by conventional methods: $P(C_2H_5)_3$, $P(C_6H_5)_2CH_3$ and $P(C_6H_5)(CH_3)_2$. The phosphines were stored under nitrogen in the glove box after the ampoules containing the materials were opened.

Triphenylphosphine was obtained from Eastman Chemicals (white label grade) and was used as received.

b) Supporting Electrolyte

Tetraethylammonium perchlorate was obtained from Eastman Chemicals (white label grade) and recrystallized three times from water. The salt was dried at 65°C under vacuum, 10^{-2} mm Hg, and stored under nitrogen in the glove box prior to use.

c) Solvents

Fisher Certified acetonitrile (500 ml) was dried by refluxing over CaH_2 for 24 hours under a nitrogen atmosphere. The acetonitrile was collected under nitrogen and stored in the glove box. This acetonitrile was used in preparative reactions. Matheson,

Coleman and Bell acetonitrile (500 ml) was also dried by refluxing over CaH_2 for 24 hours under a nitrogen atmosphere. The solvent was collected under nitrogen and stored in the glove box. This acetonitrile was principally used in polarography and voltammetry. Fisher Certified hexane (500 ml) was degassed and stored in the glove box. The 2-methoxyethanol was purchased from Sargent-Welch Chemical Company and was used as received.

d) Miscellaneous

Ruthenium trichloride trihydrate was obtained from the Alfa Division of Ventron Corporation. Silver nitrate (Fisher Reagent Grade) was used without further purification.

3. Synthesis of Ruthenium (II) Complexes

a) Preparation of chlorocarbonylhydridotris(triphenylphosphine) ruthenium (II), $Ru(H)(CO)(Cl)((C_6H_5)_3P)_3$.

The method described by Vaska (5) was utilized. Ruthenium trichloride trihydrate (1.0 g, 3.8 mmoles) was dissolved in 2-methoxyethanol (300 ml) with a six-fold excess of triphenylphosphine (6.4 g, 23 mmoles). The mixture was refluxed and stirred for 12 hours in the absence of light. The reaction mixture was allowed to cool and the solution was stirred for an additional 2 hours. The cream colored solid which formed was removed by filtration and washed with ethanol, water, ethanol and lastly light petroleum ether (b.p. 30-60°C). The product was dried under vacuum, 10^{-2} mm Hg, for 24 hours at 65°C. The yield was 2.50 g (70%).

Fig. 1

Infrared spectrum of

$Ru(H)(CO)(Cl)(Ph_3P)_3$

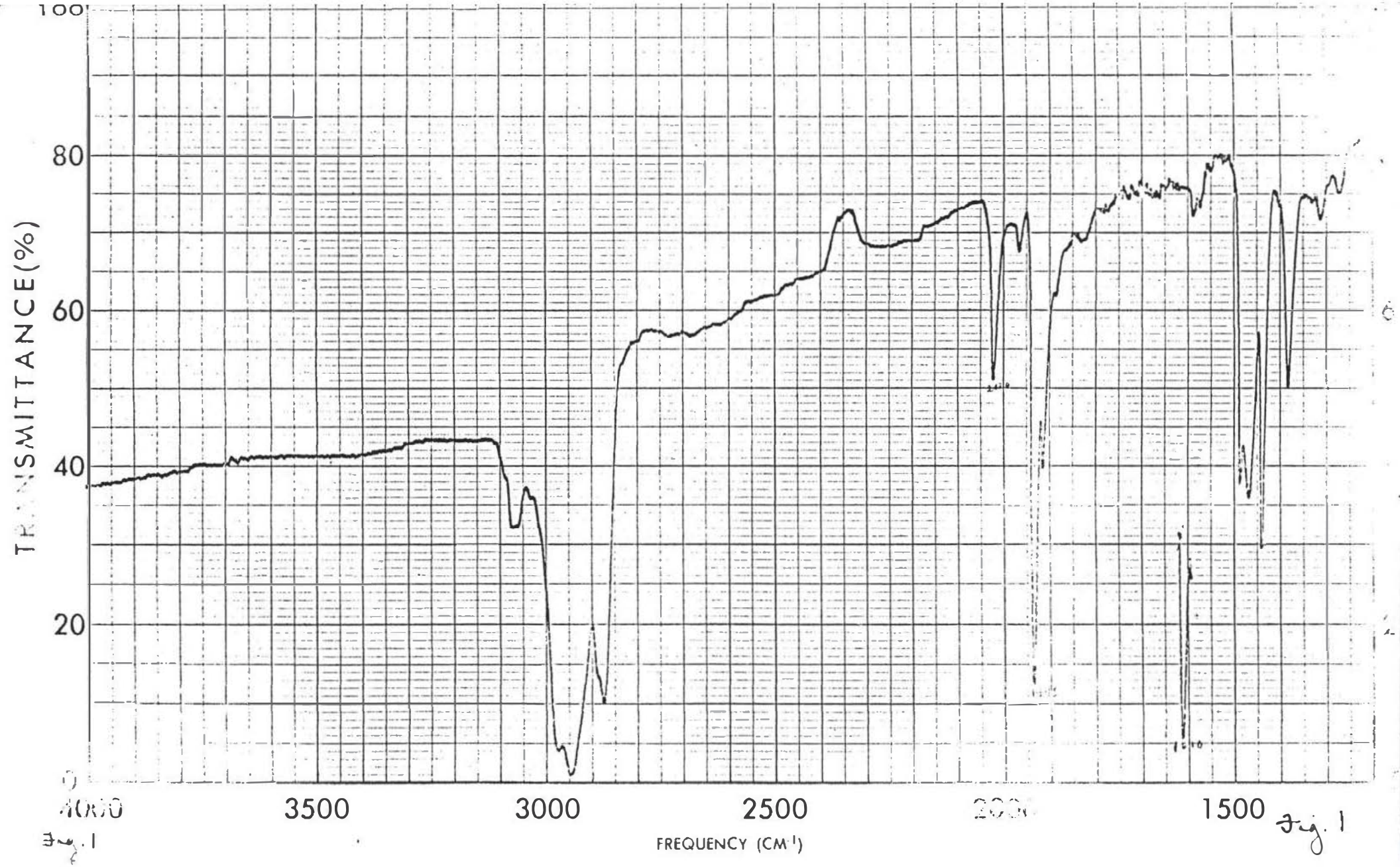
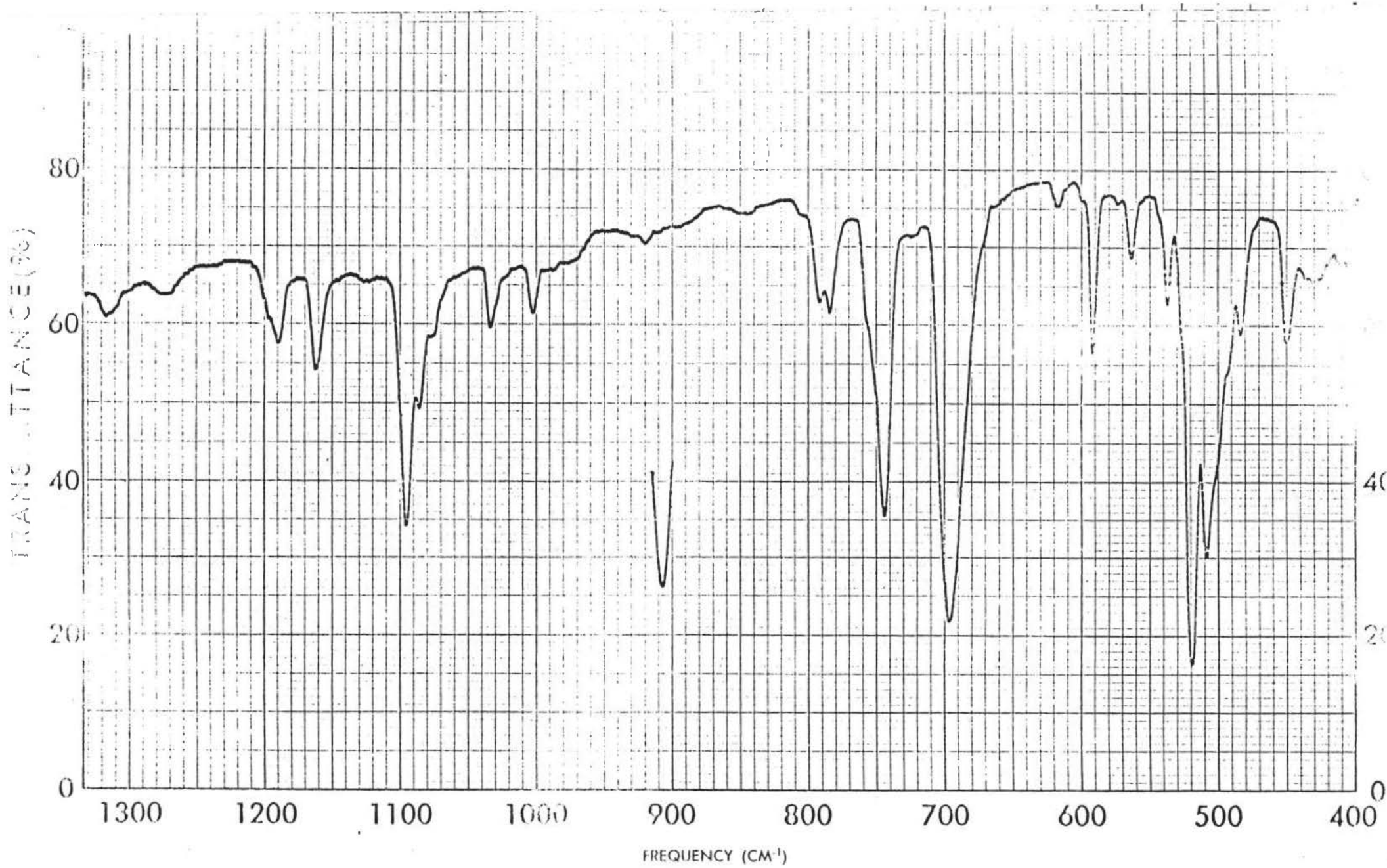


Fig. 1

Fig. 1

SAMPLE $RuHCO(CO)_2(Ph_3P)_3$	CURVE NO.	SCAN SPEED	OPERATOR
	CONC.	SLIT	DATE 1/2/71
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		



SAMPLE $Ru(II)Cl(CO)(PPh_3)_3$	CURVE NO.	SCAN SPEED	OPERATOR
ORIGIN	CODE	SLIT	DATE 1/2/8
	CELL PATH	REMARKS	

The melting point was 165-167°C (lit: 170°C) and the infrared spectrum (Fig.1) exhibited characteristic bands at 2011 cm^{-1}, ν(Ru-H), and at 1936 cm^{-1}, ν(C≡O).

b) Preparation of dichlorocarbonyltris(triphenylphosphine) ruthenium (II), $Ru(CO)(Cl)_2((C_6H_5)_3P)_3$.

To 200 ml of degassed methylene chloride was added $Ru(H)(Cl)(CO)(Ph_3P)_3$ (2.0 g, 2.03 mmoles) and then 1:1 ethanolic HCl (0.5 ml, 5.0 mmoles) was added dropwise to the stirred suspension under nitrogen. A bright yellow solution formed upon addition of the HCl. The solution was stirred for 1 hour after the HCl addition was complete. The methylene chloride solution was washed three times with 50 ml portions of H_2O and dried over anhydrous $MgSO_4$. The dry solution was reduced to dryness under vacuum, yielding orange-yellow crystals. These crystals were recrystallized from warm CH_2Cl_2. The solution was again reduced to dryness under vacuum. The yield was 1.61 g (80%). The infrared spectrum (Fig.2) showed a very strong band at 1955 cm^{-1}, ν(C≡O) as well as bands attributable to the triphenylphosphine ligand. The crystals melted at 210-215°C. Calculated for $Ru(CO)(Cl)_2(Ph_3P)_3$: C,66.94; H,4.60; P,9.42%. Found: C,66.74; H,4.75; P,9.61%.

c) Preparation of dichlorocarbonylbis(triphenylphosphine) ruthenium (II), $Ru(CO)(Cl)_2((C_6H_5)_3P)_2$.

The following three methods produced solids with the

Fig. 2

Infrared spectrum of

$Ru(CO)(Cl)_2((C_6H_5)_3P)_3$

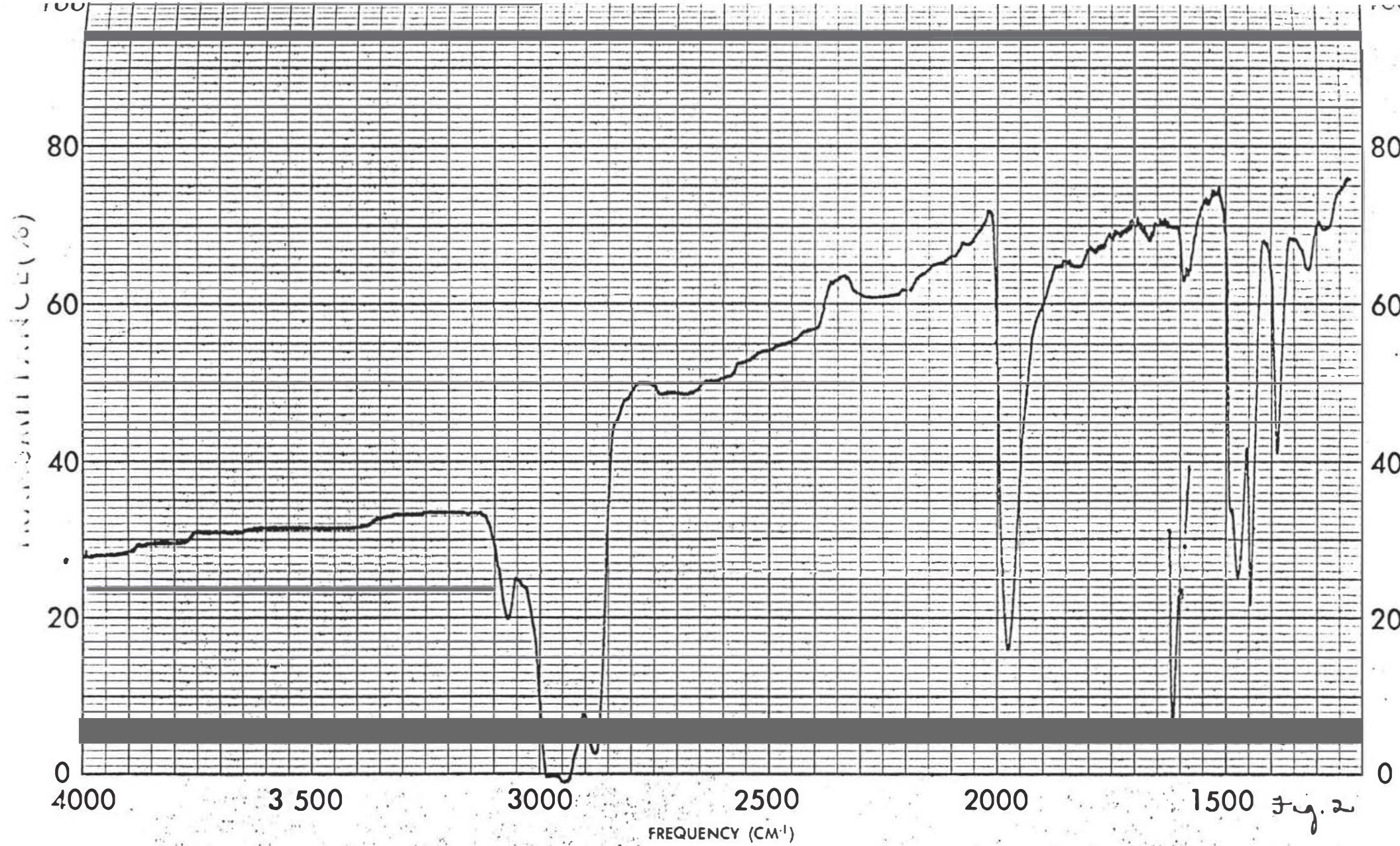
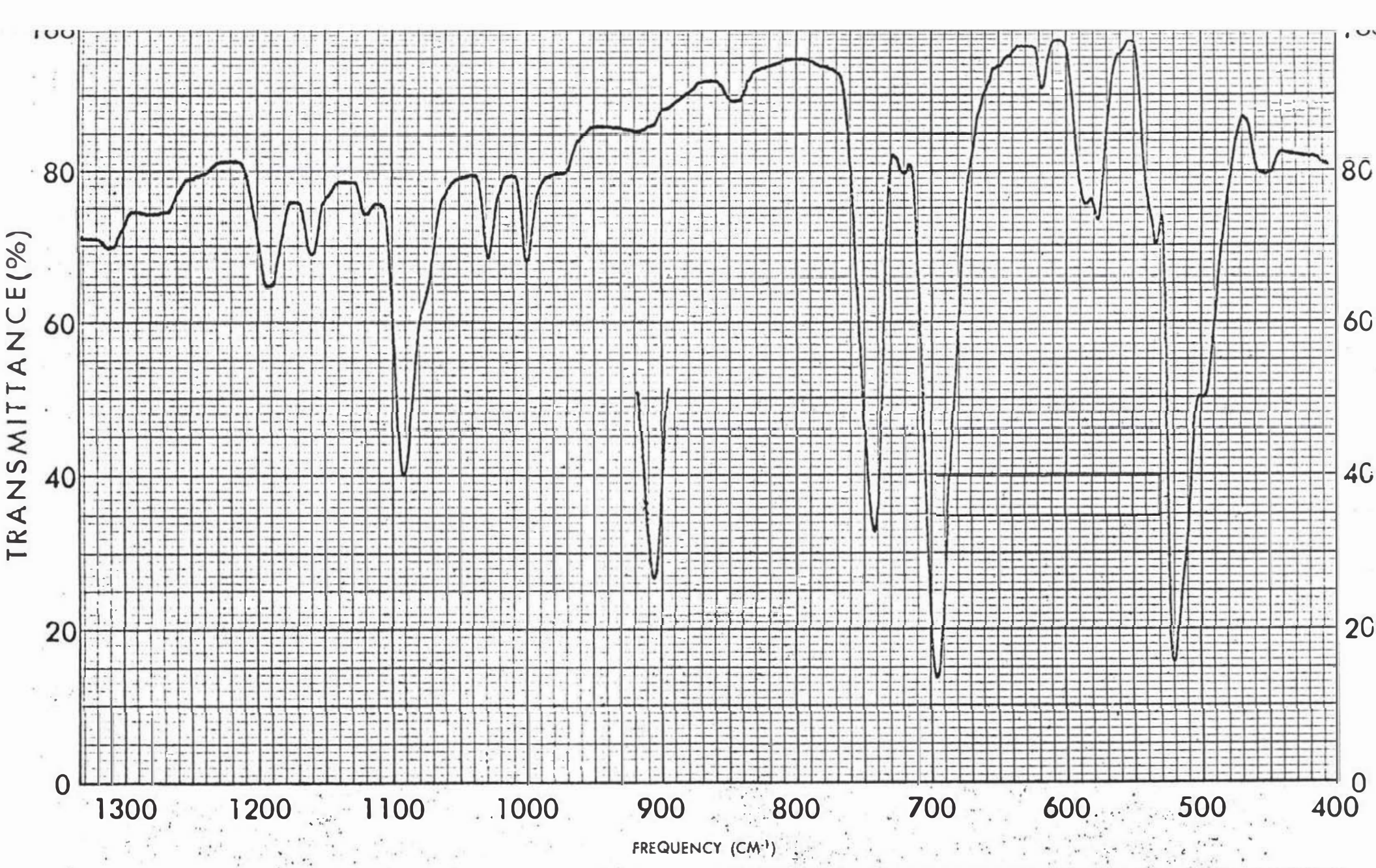


Fig. 2

SAMPLE $Ru(CO)Cl_2(Ph_3P)_3$	CURVE NO.	SCAN SPEED	OPERATOR
	CONC.	SLIT	DATE 1/2/81
ORIGIN	CELL PATH	REMARKS: Nujol mull	
SOLVENT	REFERENCE		



SAMPLE $RuCl_2(\phi_3P)_3$	CURVE NO.	SCAN SPEED	OPERATOR
	CONC.	SLIT	DATE 1/2/81
ORIGIN	CELL PATH	REMARKS new sample	
SOLVENT	REFERENCE		

empirical formula, $Ru(CO)(Cl)_2(Ph_3P)_2$.

(1) Method 1

The filtrate remaining after the removal of $Ru(H)(CO)(Cl)(Ph_3P)_3$ (vide infra) by filtration was distilled under vacuum to remove the 2-methoxyethanol solvent. A red-orange oil was obtained which upon standing overnight formed orange crystals. The crystals were then washed three times with hot hexane (75 ml) to remove excess triphenylphosphine. The remaining orange solid was dried under vacuum and treated with hot 95% ethanol. The solid material became yellow in color and the supernatant ethanol solution was pale yellow in color. The ethanol suspension was cooled to $-12^{o}C$ and the yellow product removed by filtration and washed with ethanol. The yellow powder was dried at $55^{o}C$ at a pressure of 10^{-2} mm Hg for 12 hours. Upon drying the yellow powder changed color to reddish-brown but upon standing at room temperature the color returned to yellow. The yield was 45% (0.58 g) based on the original ruthenium complex that was charged. The infrared spectrum (Fig.3) exhibited a strong band at 1955 cm^{-1}, $\nu(C\equiv O)$. The solid melted to a red liquid in the range 198-200°C. Calculated for $Ru(CO)(Cl)_2(Ph_3P)_2$(A): C,61.33; H,4.19; P,8.56%. Found: C,61.05; H,4.40; P,8.41%.

(2) Method 2

A 0.100 g (0.138 mmoles) sample of $Ru(CO)(Cl)_2(Ph_3P)_2$(A) was treated with 10 ml of CH_3CN. The solvent slowly became yellow and the solid also began to become more yellow as the solution was shaken by hand. After 5-10 minutes, a bright yellow-green solid was formed. The supernatant liquid was very

Fig.3

Infrared spectrum of

$Ru(CO)(Cl)_2(Ph_3P)_2$(A)

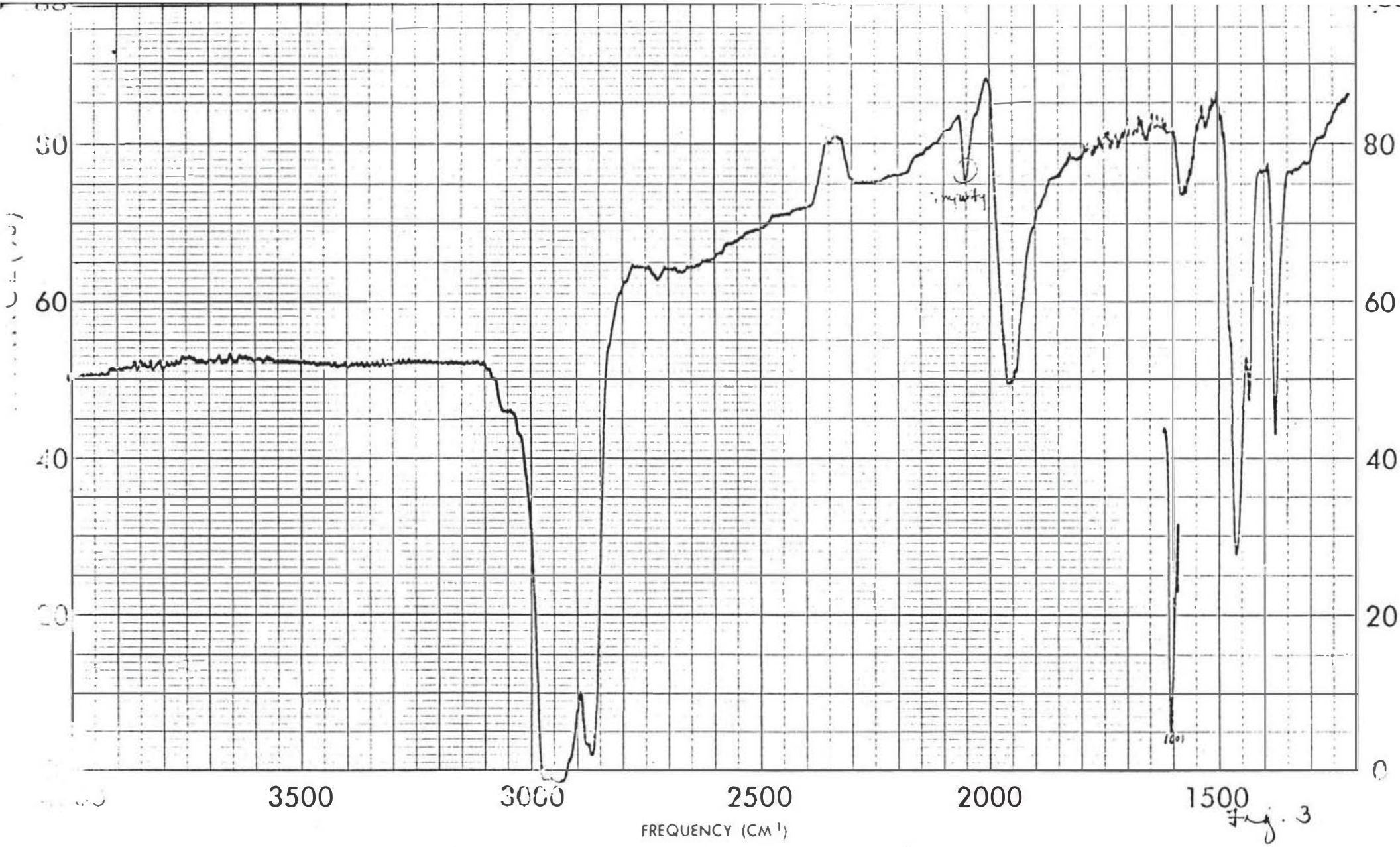
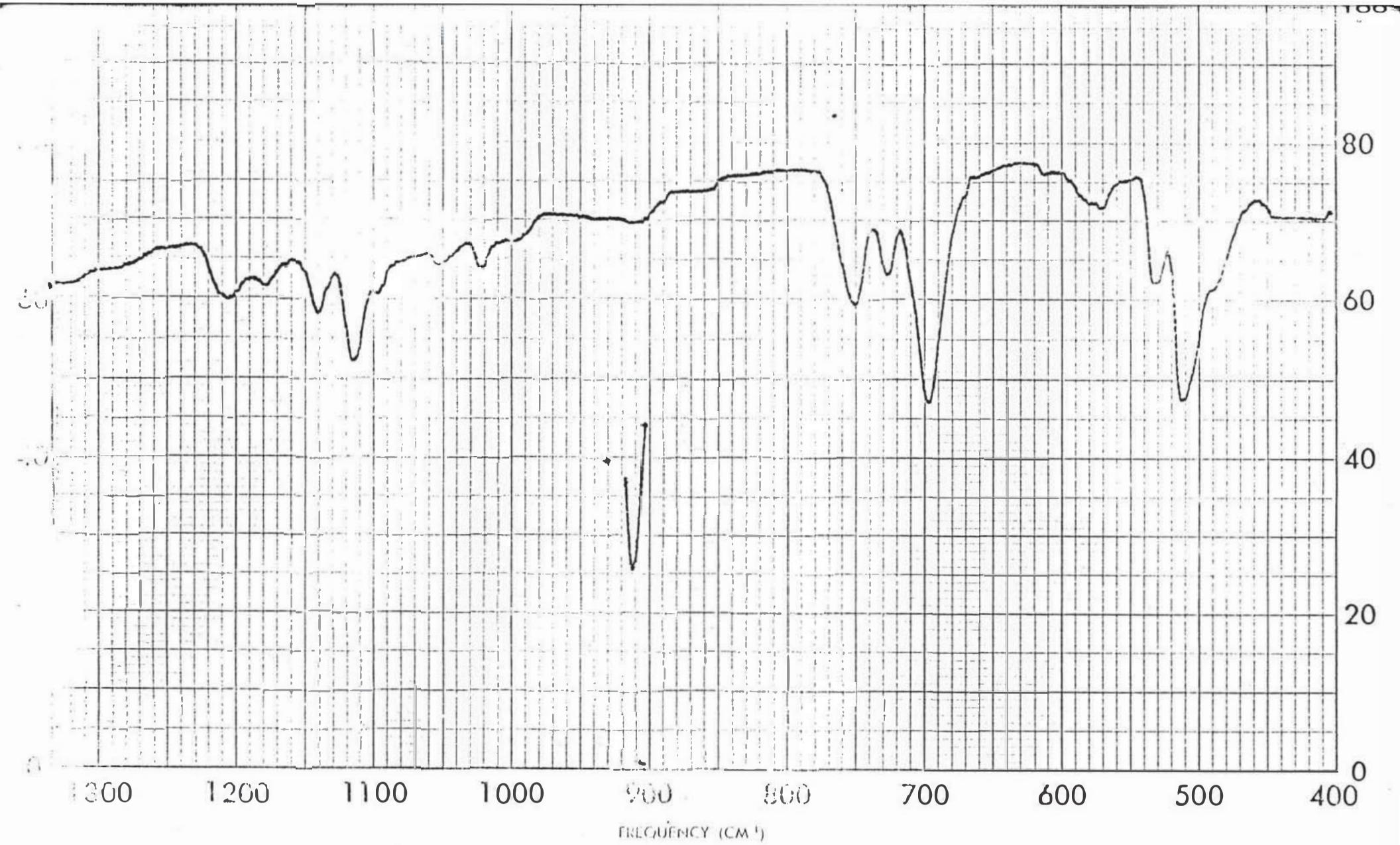


Fig. 3

SAMPLE [illegible] (cyclohexane solid)	CURVE NO.	SCAN SPEED	OPERATOR
	CONC.	SLIT	DATE
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		



#1 yellow solid

CURVE NO
CONC.
CELL PATH
REFERENCE

SCAN SPEED
SLIT
REMARKS

OPERATOR
DATE 1/1/81

Fig.4

Infrared spectrum of

$Ru(CO)(Cl)_2(Ph_3P)_2$(B)

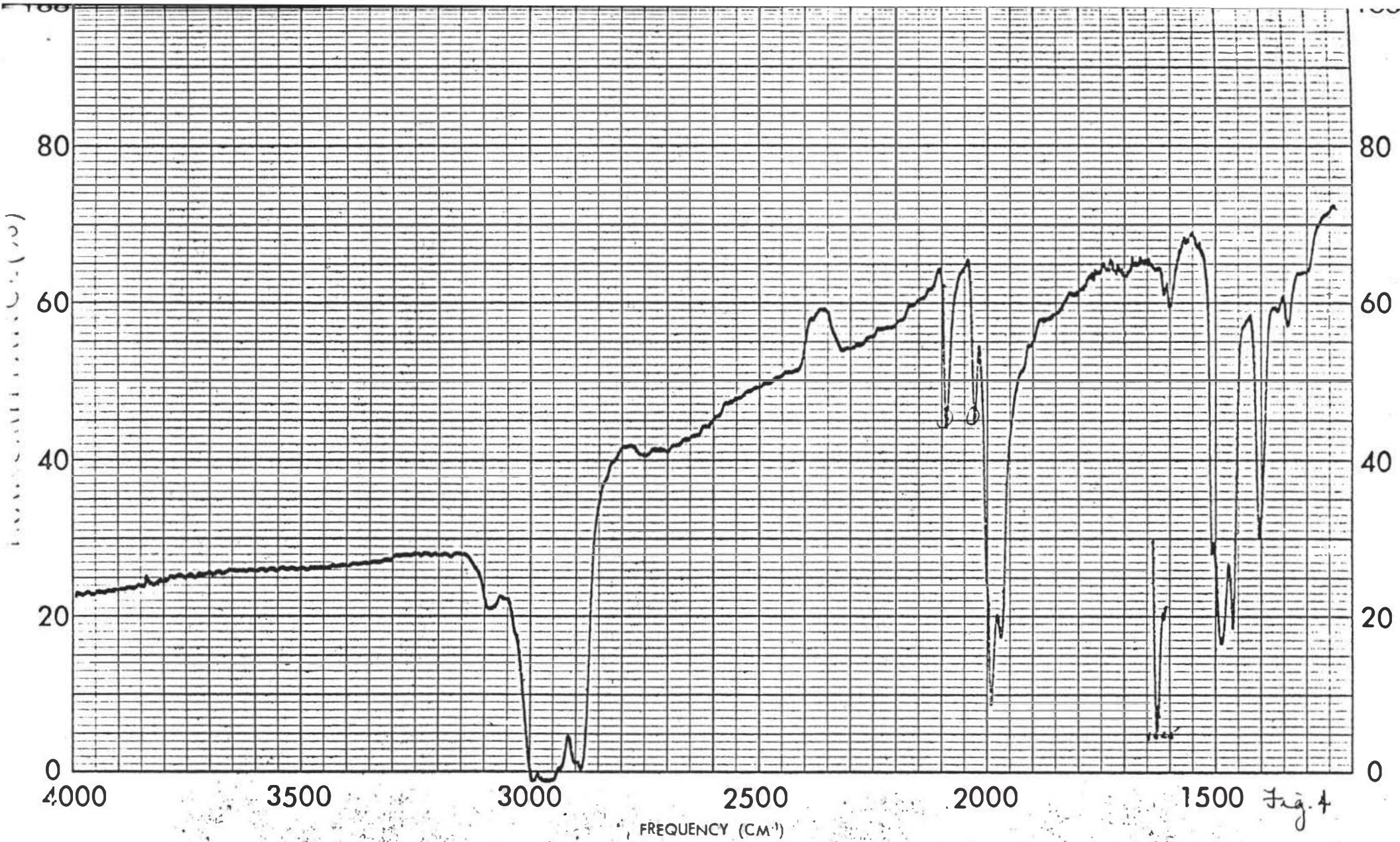
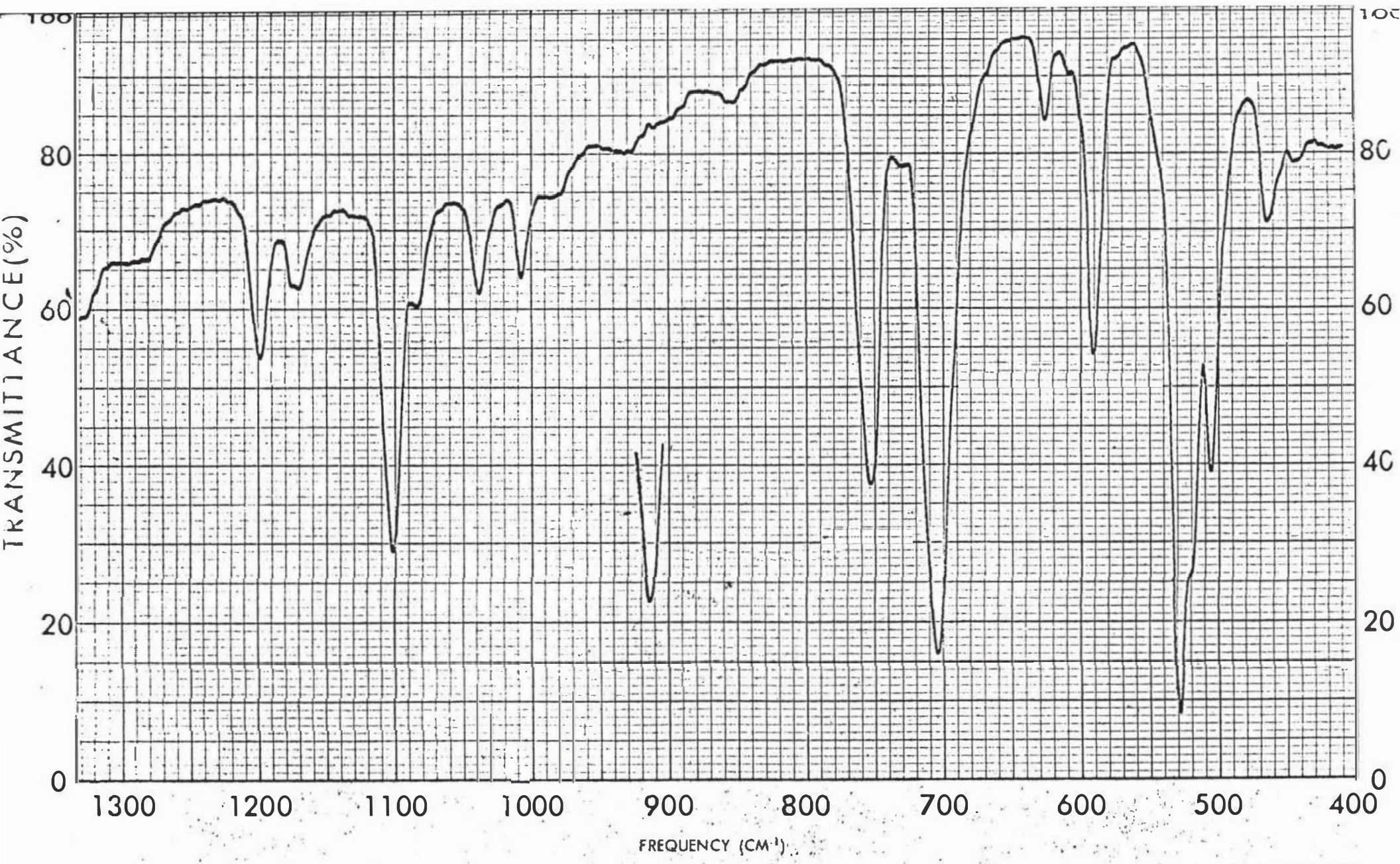


Fig. 4

SAMPLE 79-1 (yellow solid)	CURVE NO.	SCAN SPEED fast	OPERATOR J. Bady
	CONC.	SLIT N	DATE 1/8/81
ORIGIN	CELL PATH	REMARKS	
SOLVENT Nujol mull	REFERENCE air		



SAMPLE 79-1 (yellow solid)	CURVE NO.	SCAN SPEED fast	OPERATOR J Bady
	CONC.	SLIT N	DATE 1/8/81
ORIGIN	CELL PATH	REMARKS	
SOLVENT Nujol mull	REFERENCE polystyrene		

pale yellow. The crystals were filtered and washed well with CH_3CN. They were dried at room temperature under vacuum (10^{-2} mm Hg) for 2 hours. The collected yield was 93% (0.09 g). The infrared spectrum (Fig.4) showed two prominent bands at 1945 and 1960 cm^{-1}, $\nu(C\equiv O)$. The bands at 2061 and 2000 cm^{-1} are indicative of a mixture of products. This impurity may be $Ru(H)(Cl)(CO)(Ph_3P)_3$ or a derivative of this material. The yellow-green crystals decomposed to a red liquid at 244°C. Calculated for $Ru(CO)(Cl)_2(Ph_3P)_2$(B): C,61.33; H,4.19; P,8.56%. Found: C,61.11; H,4.43; P,8.25%.

(3) Method 3

In 15 ml of acetonitrile, $Ru(CO)(Cl)_2(Ph_3P)_3$ (0.493 g, 0.500 mmoles) was stirred for 2 hours under nitrogen in the glove box. Yellow-green crystals were formed from the reaction. The crystals were washed with CH_3CN and filtered. They were then dried under vacuum (10^{-2} mm Hg) at room temperature. The yield was 92% (0.366 g). In the infrared spectrum (Fig.5) there was observed two strong bands at 1945 and 1961 cm^{-1}, $\nu(C\equiv O)$. The crystals melted to a red liquid in a range of 245-250°C. Calculated for $Ru(CO)(Cl)_2(Ph_3P)_2$(C): C,61.33; H,4.19; P,8.56%. Found: C,61.47; H,4.42; P,8.19%.

The combined supernatant liquid and washes from the above reaction were reduced to dryness under vacuum yielding a beige residue. This material was extracted with hot hexane. Reduction of the hexane extract under vacuum yielded white crystals of triphenylphosphine (0.100 g) which were identified by the

Fig.5

Infrared spectrum of

$Ru(CO)(Cl)_2(Ph_3P)_2(C)$

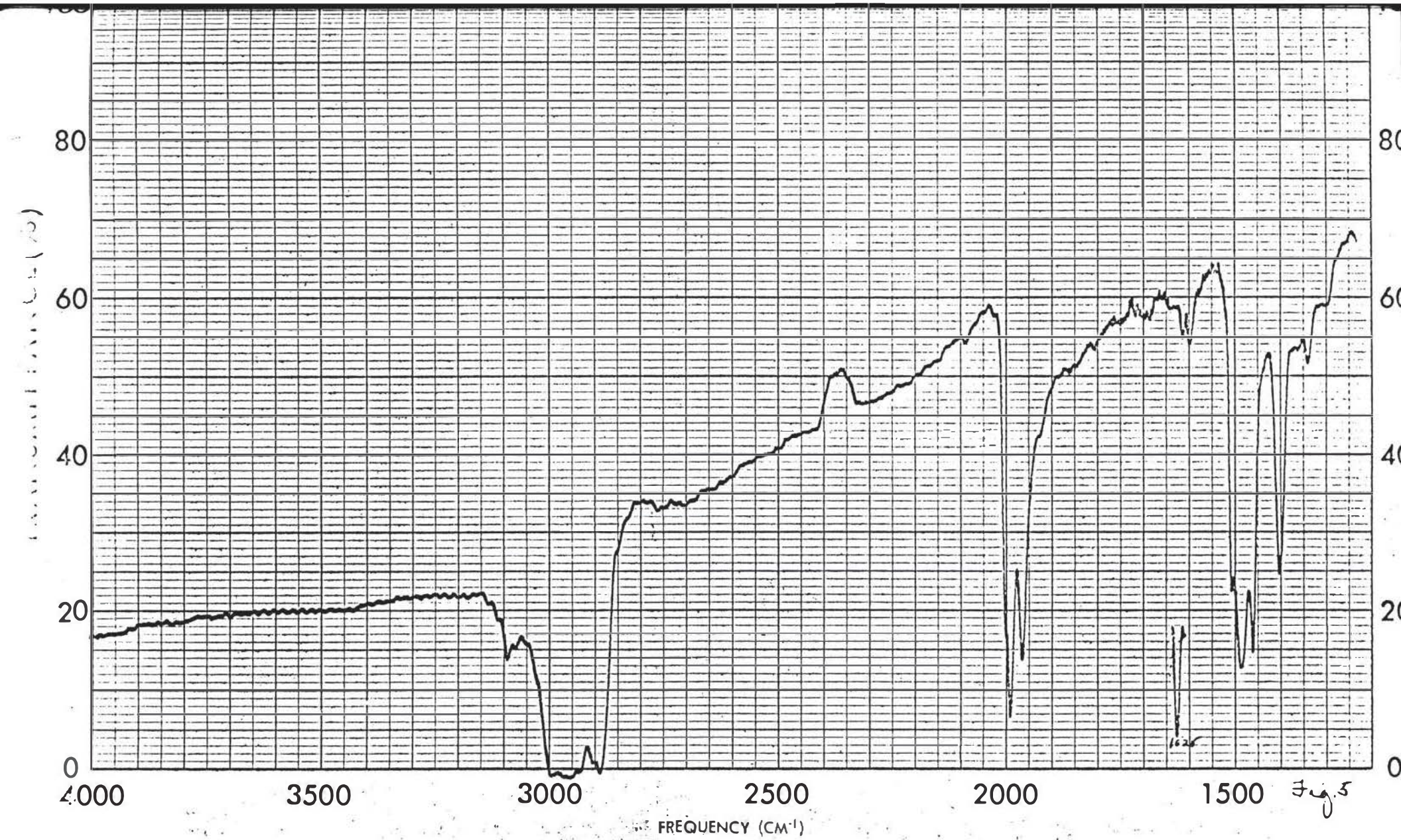
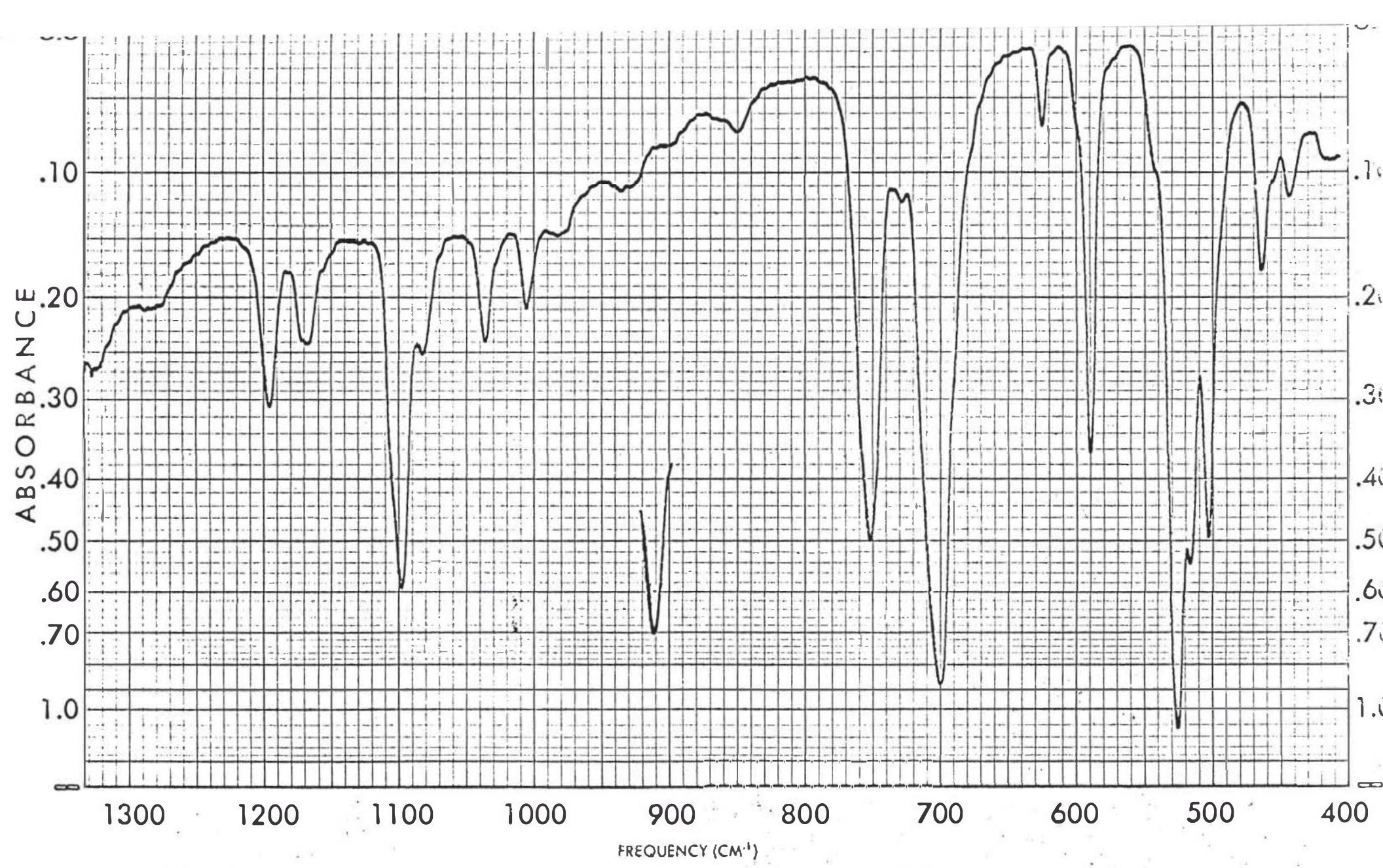


Fig. 5

SAMPLE 90-1	CURVE NO.	SCAN SPEED fast	OPERATOR J. Bailey
	CONC.	SLIT	DATE 1/14/81
ORIGIN	CELL PATH	REMARKS yellow crystals from $RuCO(H)_2(\phi_3P)_2$ in CH_2Cl_2	
SOLVENT	REFERENCE		

PR 1122 (337-1203)



SAMPLE 80-1	CURVE NO.	SCAN SPEED Fast	OPERATOR D. Body
	CONC.	SLIT	DATE 1/14/81
ORIGIN	CELL PATH	REMARKS yellow crystals from	
SOLVENT	REFERENCE	$RuCl_2(\phi_3P)_3$ in CH_3CN	

the melting point, 79-80°C (Lit. value: 80°C). The amount of triphenylphosphine isolated corresponds to a 76% recovery of that expected from ligand loss from the initial starting complex.

d) Preparation of tri-μ-chlorohexakis(diphenylmethylphosphine) diruthenium (II) chloride, $(Ru_2Cl_3((C_6H_5)_2CH_3P)_6)Cl$.

The method of Chatt and Hayter (6) was used to prepare this compound. To a sample of $RuCl_3$ (1.60 g, 7.71 mmoles), 49.6 ml of H_2O was added. To this solution diphenylmethylphosphine (6.54 ml, 34.8 mmoles) and 149 ml of methanol were added and the mixture refluxed under nitrogen for 24 hours. The color of the solution went from dark brown through muddy green to bright orange. The volume of the solution was reduced to about half under vacuum (10^{-2} mm Hg), after which yellow crystals formed. The crystals were filtered and washed thoroughly with methanol and dried at room temperture under vacuum. The resulting powder was canary yellow in color. The yield obtained was 92% (4.82 g). The infrared spectrum (Fig.6) showed characteristic phosphine stretches from 900 to 400 cm^{-1}. The melting point of the crystals was in a range 140-142°C (d).

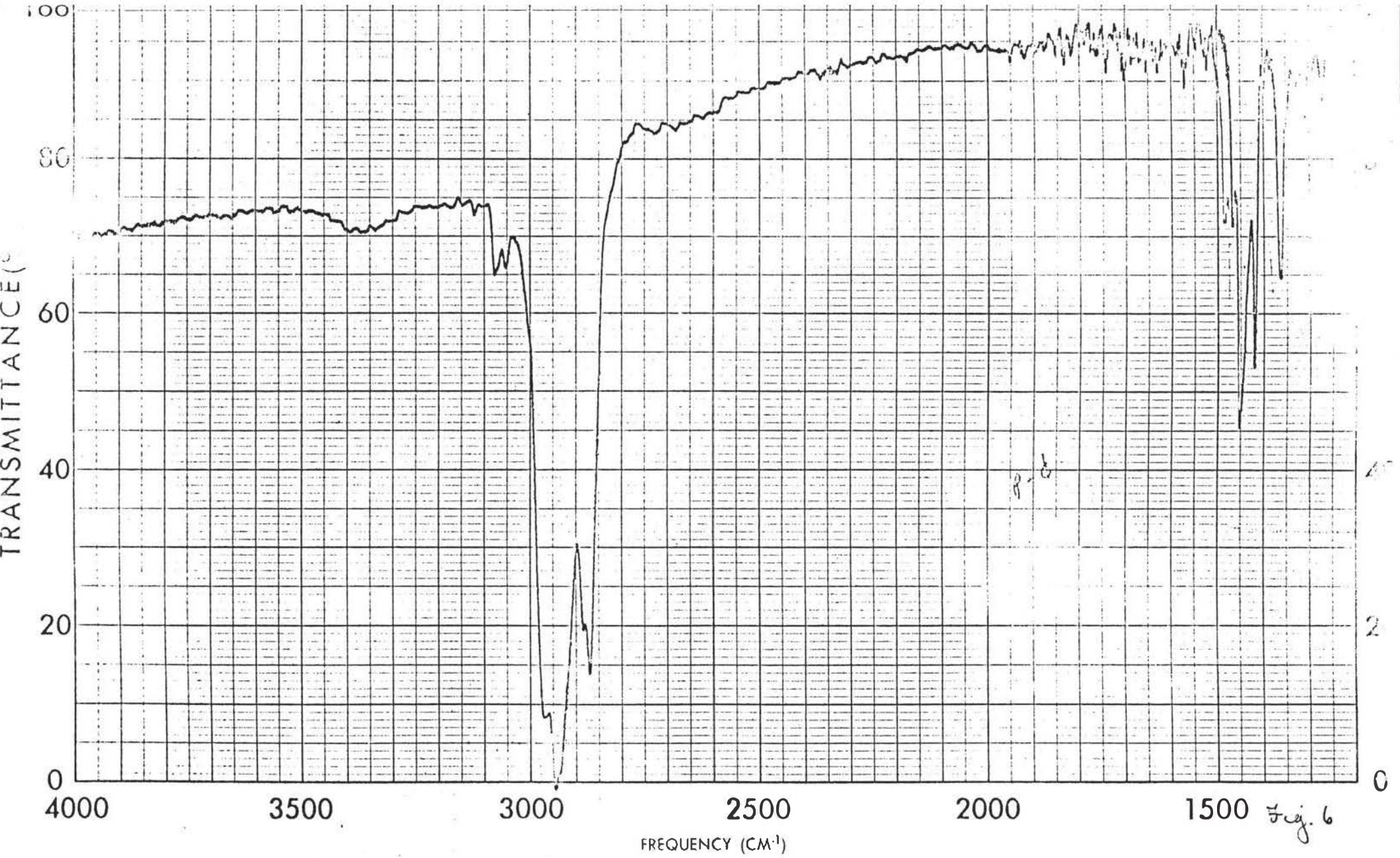
e) Preparation of tri-μ-chlorohexakis(dimethylphenylphosphine) diruthenium (II) chloride, $(Ru_2Cl_3((C_6H_5)(CH_3)_2P)_6)Cl$.

By the method described by Chatt and Hayter (6), 0.801 g (3.86 mmoles) of $RuCl_3 \cdot 3H_2O$ was dissolved in 24.8 ml of H_2O.

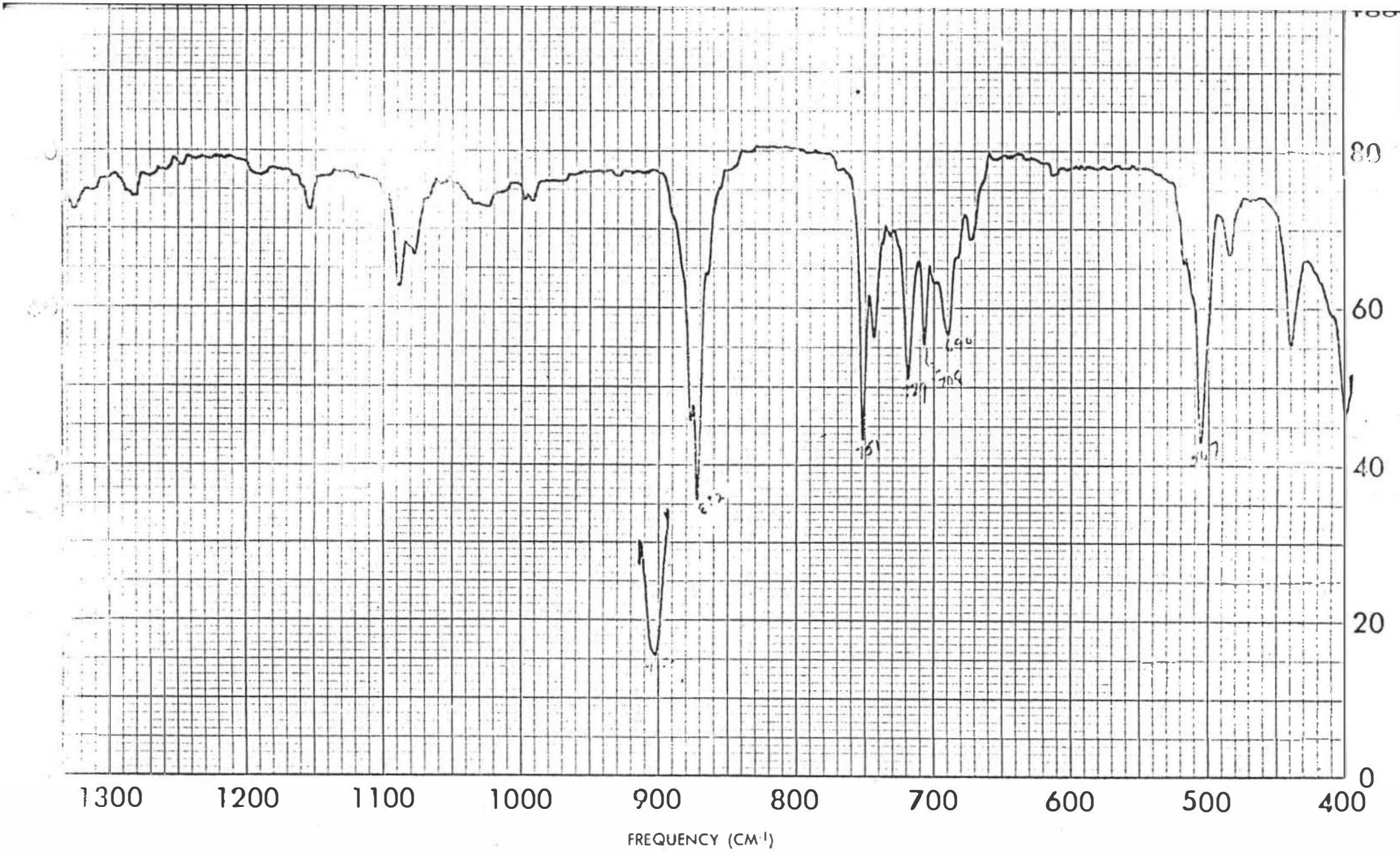
Fig.6

Infrared spectrum of

$(Ru_2Cl_3((C_6H_5)_2(CH_3)P)_6)Cl$



SAMPLE [illegible]	CURVE NO.	SCAN SPEED Dark	OPERATOR
	CONC.	SLIT	DATE
ORIGIN	CELL PATH	REMARKS	



sample Et_2O, (q, in CCl_4)	CURVE NO.	SCAN SPEED	OPERATOR
	CONC.	SLIT	DATE
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		

Dimethylphenylphosphine (2.48 ml, 17.4 mmoles) and 74.6 ml of methanol were added and the mixture refluxed under nitrogen with stirring for 24 hours. The solution color went from dark brown to red-brown and finally to clear orange. After refluxing, the solution was reduced to half its volume under vacuum and yellow crystals precipitated from the solution. The crystals were filtered and washed with a 1:1 v/v mixture of methanol and water. The crystals were dried under vacuum. The weight of the crystals was 1.59 g, 80% yield. The infrared spectrum (Fig.7) indicated characteristic phosphine stretches in the fingerprint region. The melting point of the crystals was 82-86°C (d).

f) Preparation of dichlorocarbonyltris(diphenylmethylphosphine) ruthenium (II), $RuCl_2(CO)((C_6H_5)_2CH_3P)_3$.

Two procedures were utilized in synthesizing this complex. The first procedure used was an extension of a method by Chatt, Shaw and Field (7). In this method, $(Ru_2Cl_3((C_6H_5)_2CH_3P)_6)Cl$ (0.66 g, 0.43 mmoles) was refluxed in boiling ethanol (20 ml) and 2 ml of 1M KOH for 45 minutes under nitrogen. All reagents must be throughly de-gassed before use. After refluxing, the solution was cooled for 5 minutes and 5 ml of concentrated HCl was added to the solution. Addition of the acid caused effervescence and a beige precipitate formed. This tan solid was separated by filtration and recrystallization from ethanol gave white crystals. The weight of recrystallized product was 0.32 g (93% yield). The infrared spectrum (Fig.8) exhibited two bands at 1938 and 1952 cm^{-1},

Fig.7

Infrared spectrum of

$(Ru_2Cl_3(PhMe_2P)_6)Cl$

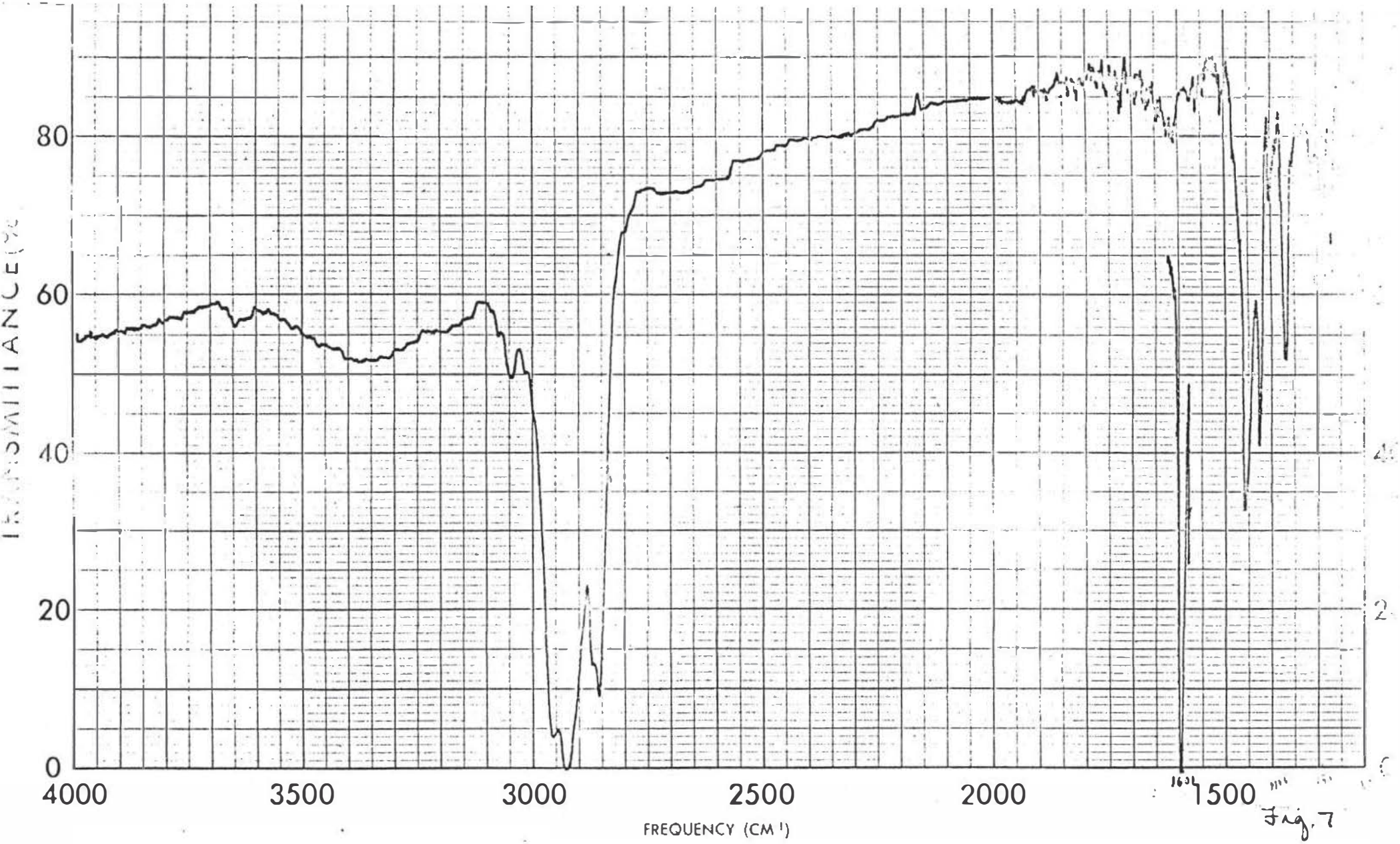
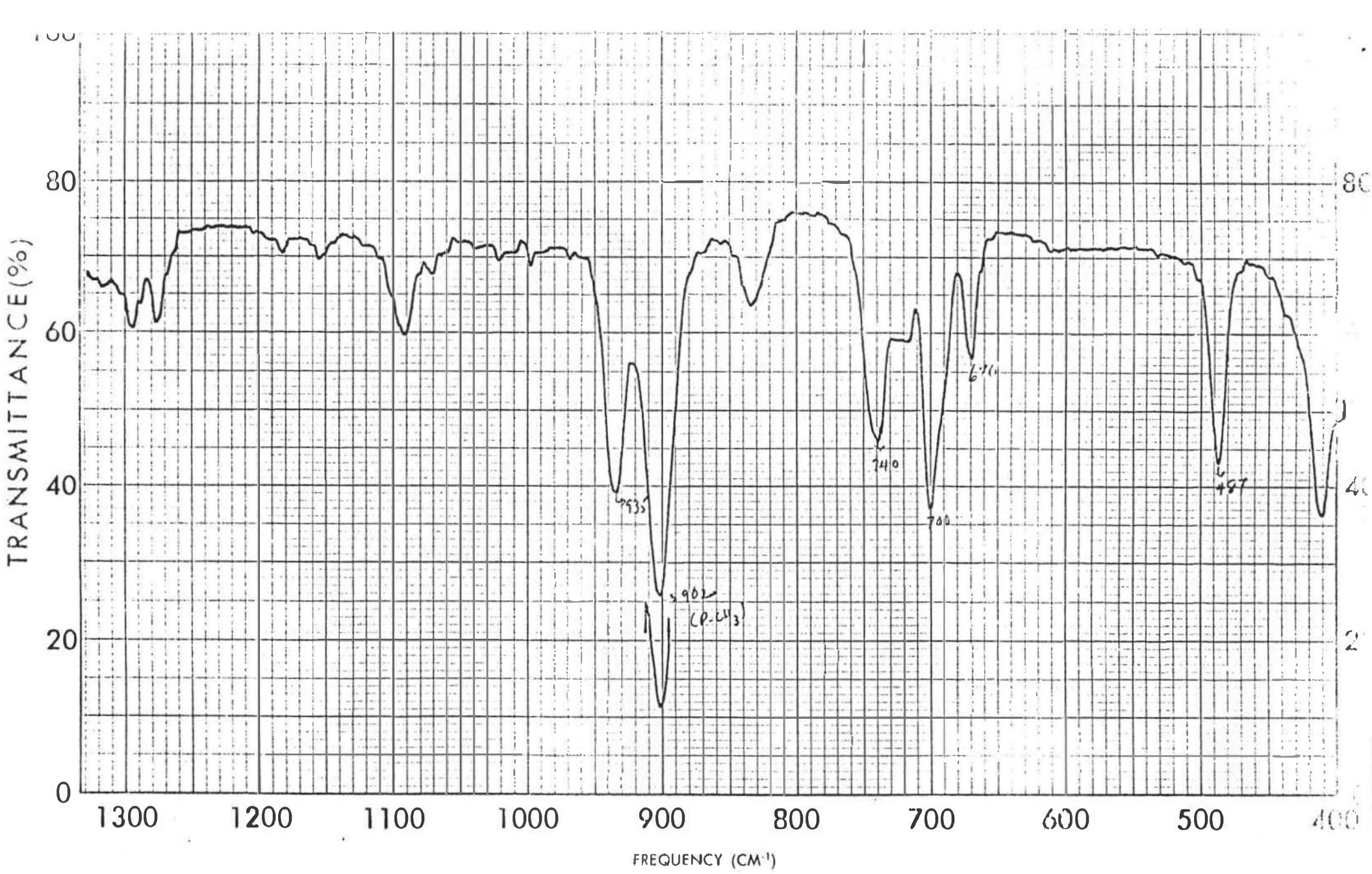


Fig. 7

SAMPLE. $Ru_2Cl_3(Ome_2P)_6]Cl$	CURVE NO.	SCAN SPEED	OPERATOR
	CONC.	SLIT	DATE
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		



SAMPLE $[Ru_2Cl_3(\phi Me_2P)_4]Cl$	CURVE NO.	SCAN SPEED fast	OPERATOR
	CONC.	SLIT	DATE 1/12
	CELL PATH	REMARKS	

Fig.8

Infrared spectrum of

$Ru(CO)(Cl)_2(Ph_2MeP)_3$

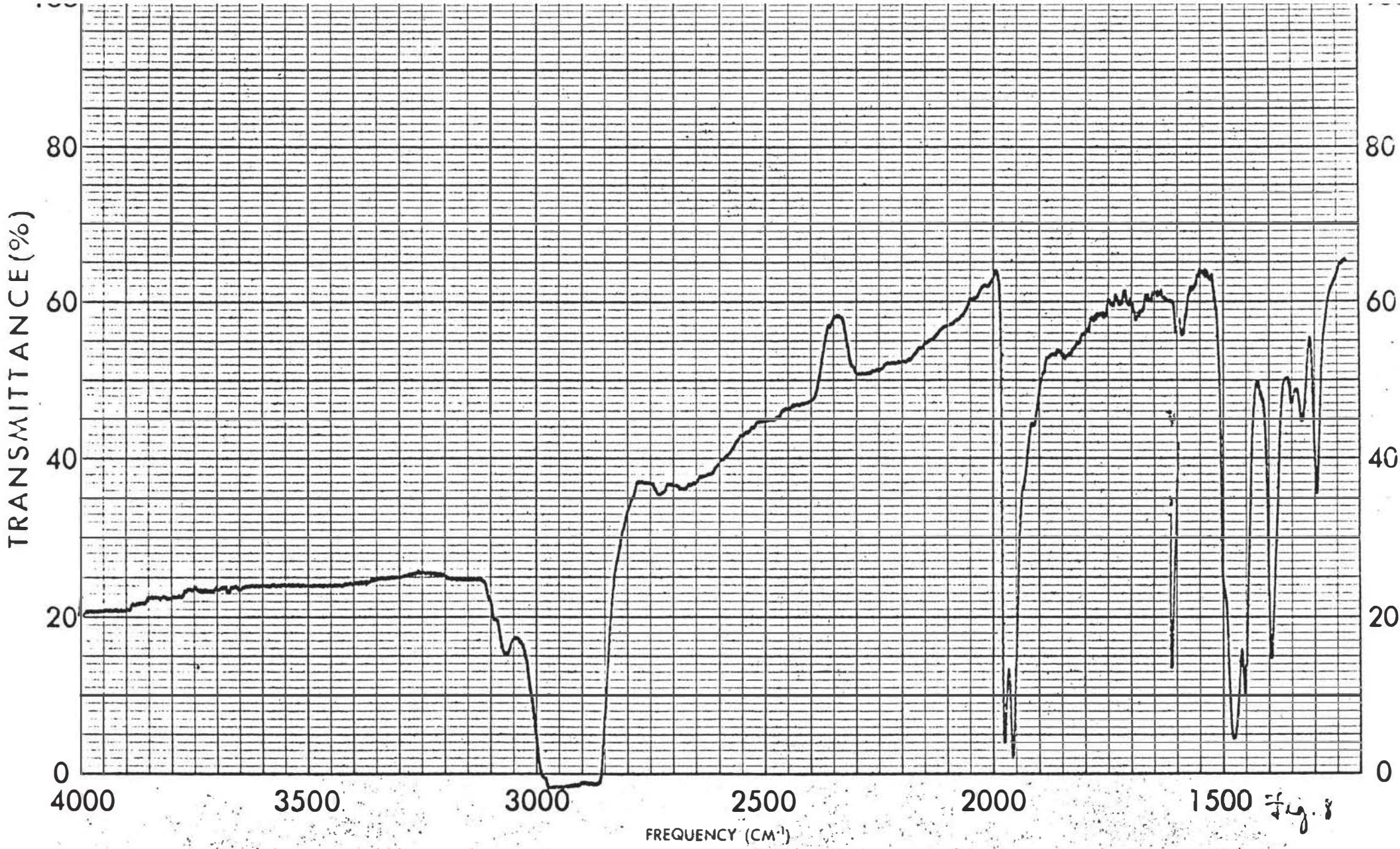
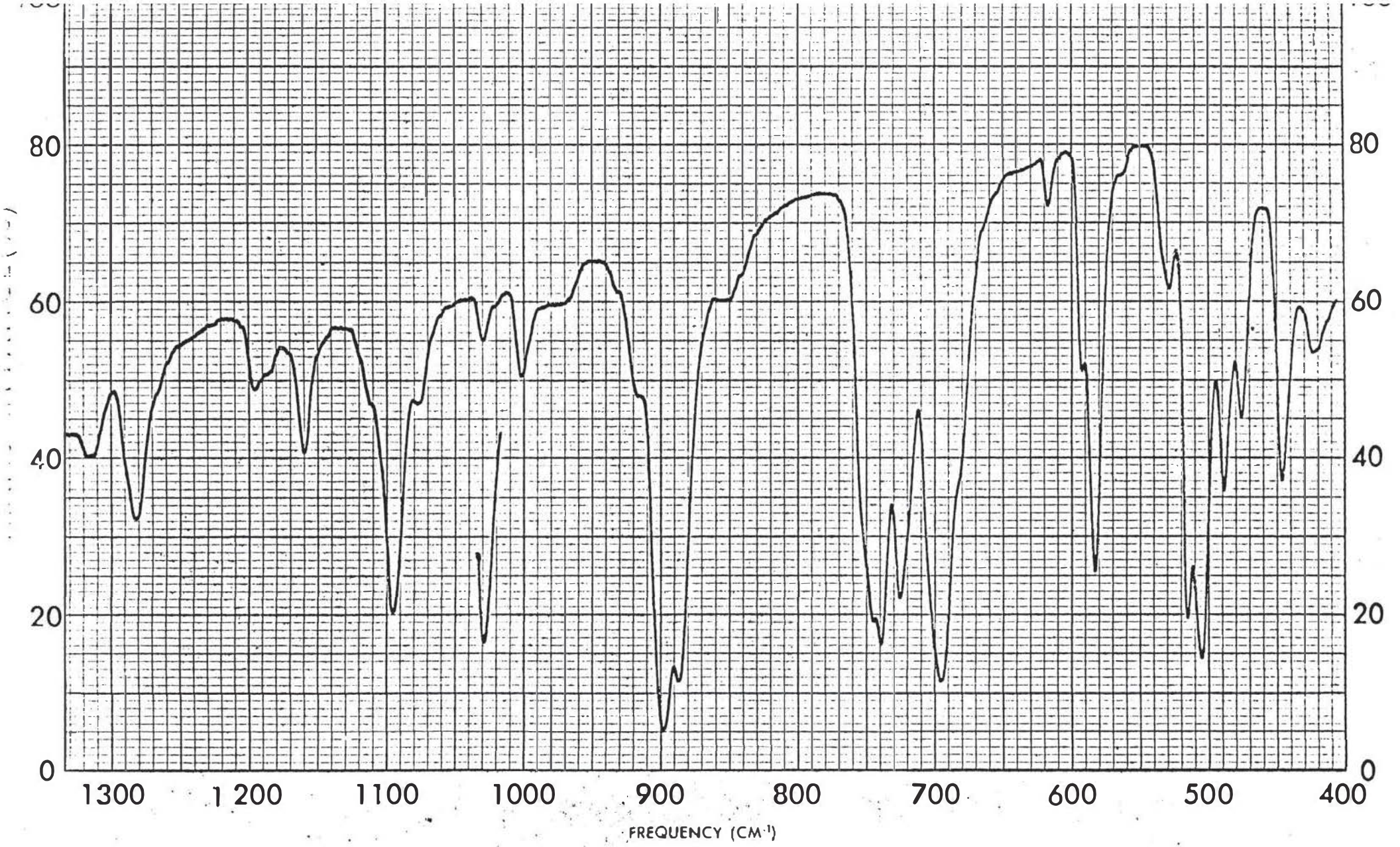


Fig. 8

SAMPLE $RuCO(Cl_2)(\phi_2MeP)_3$	CURVE NO.	SCAN SPEED	OPERATOR D. L. Thorn
	CONC.	SLIT	DATE 12/30/80
ORIGIN	CELL PATH	REMARKS Nit grey	
SOLVENT	REFERENCE		



SAMPLE $Ru CoCl_2(\phi_2 MeP)_3$	CURVE NO.	SCAN SPEED	OPERATOR D.A. Sherman
	CONC.	SLIT	DATE 12/30/80
ORIGIN	CELL PATH	REMARKS lit prep.	
SOLVENT	REFERENCE		

$\upsilon(C\equiv O)$. The melting point range of the solid was 225-230°C yielding a yellow liquid.

The second procedure, for the production of this compound, was an extension of a method of Armit and Stephenson (8). A 0.500 g (0.507 mmoles) sample of $Ru(CO)(Cl)_2(Ph_3P)_3$ was refluxed and stirred under nitrogen with a six-fold excess of Ph_2MeP (0.571 ml, 3.04 mmoles) and 50 ml of degassed hexane for 10 hours. The solid in this suspension changed from a bright yellow to an off-white solid. The crystals were separated by filtration and washed with hexane. They were dried under vacuum (10^{-2} mm Hg) for 12 hours at room temperture. The yield of the compound was 0.366 g (90%). The infrared spectrum (Fig.9) showed two bands at 1945 and 1954 cm^{-1}, $\upsilon(C\equiv O)$. The bands at 2061 and 2000 cm^{-1} are indicative of a mixture of products. This may be a trace of $Ru(H)(Cl)(CO)(Ph_3P)_3$ or a derivative of this material. The solid melted to a yellow liquid at 205°C. Calculated for $Ru(CO)(Cl)_2(Ph_2MeP)_3$: C,60.01; H,4.92; P,11.62%. Found: C,59.89; H,4.77; P,11.45%.

g) Preparation of dichlorocarbonyltris(dimethylphenylphosphine) ruthenium (II), $Ru(CO)(Cl)_2((CH_3)_2(C_6H_5)P)_3$.

A revised method based on the work of Armit and Stephenson (8) required $RuCl_2(CO)(Ph_3P)_3$ (0.300 g, 0.304 mmoles) to be mixed with $PhMe_2P$ (0.253 g, 1.83 mmoles, 0.261 ml) and 50 ml of degassed hexane. The mixture was refluxed and stirred for 24 hours under nitrogen. The suspended crystals went from dark yellow to powdery white. The powder was filtered, washed with hexane and dried under vacuum (10^{-2} mm Hg) for 12 hours at room temperature.

Fig.9

Infrared spectrum of

$Ru(CO)(Cl)_2(Ph_2MeP)_3$

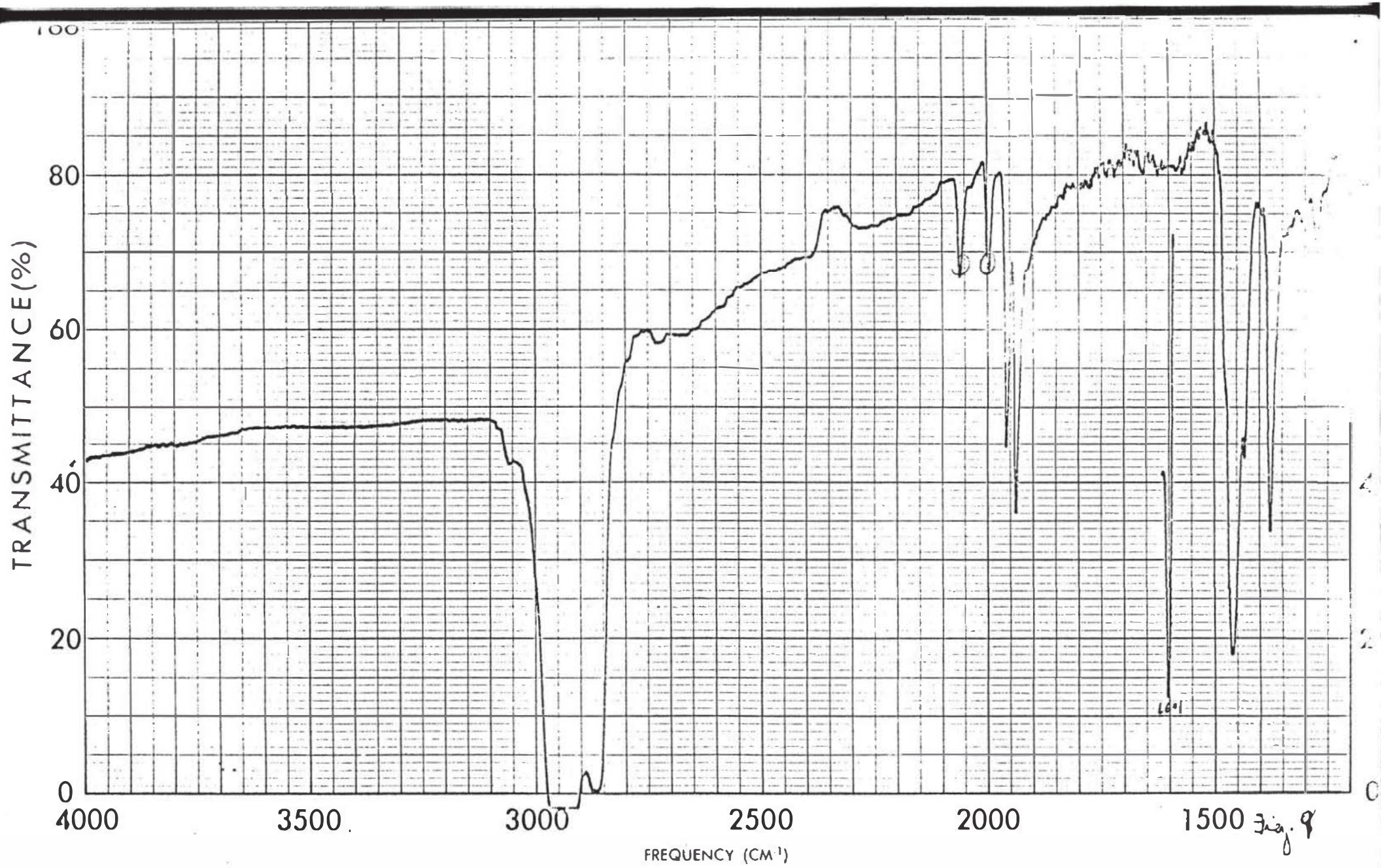
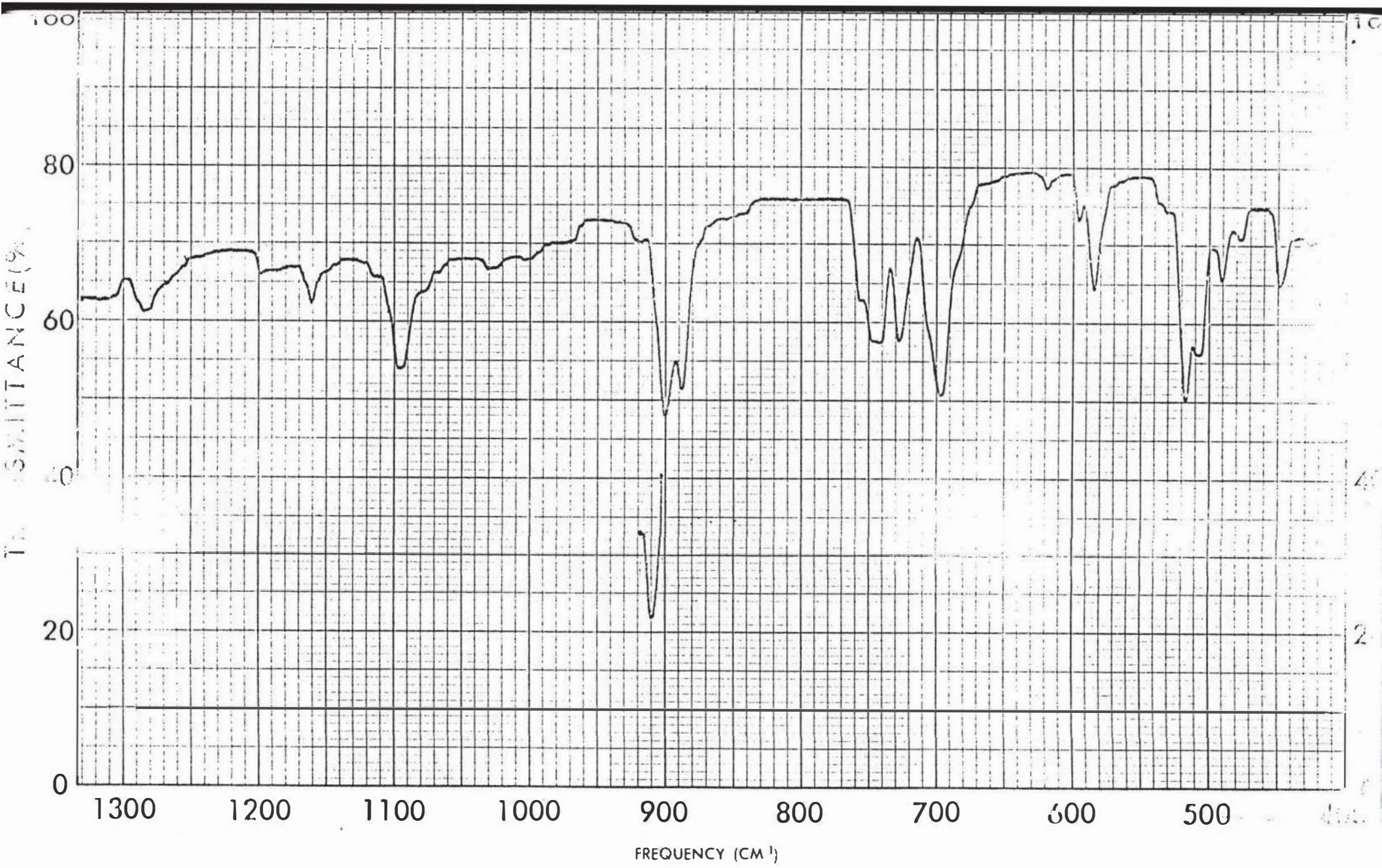


Fig. 9

SAMPLE $RuCoCl_2(\phi_2MeP)_3$	CURVE NO	SCAN SPEED Fast	OPERATOR
	CONC	SLIT	DATE 12/1/80
ORIGIN	CELL PATH	REMARKS	



SAMPLE $RuCOCl_2(\phi_3 mP)_3$	CURVE NO.	SCAN SPEED	OPERATOR
	CONC.	SLIT	DATE 12/1/80
ORIGIN	CELL PATH	REMARKS	

The yield of the compound was 0.164 g (88%). There was a strong absorption band at 1945 cm^{-1}, $\nu(C\equiv O)$, in the infrared spectrum (Fig.10). The two small bands at 2060 and 2000 cm^{-1} indicates one or more impurities in the sample. The white powder melted at 173-175°C to a yellow liquid. The literature (9) value was 179-181°C. Calculated for $Ru(CO)(Cl)_2((CH_3)_2(C_6H_5)P)_3$: C,48.86; H,5.42; P,15.12%. Found: C,48.72; H,5.64; P,14.96%.

4. Synthesis of Ruthenium (0) Complexes

a) Preparation of acetonitrilecarbonyltris(triphenylphosphine) ruthenium (0), $Ru(CO)(CH_3CN)((C_6H_5)_3P)_3$.

The procedure for the synthesis of this compound was similar to the method given by Olson (1). The reaction was performed in the nitrogen atmosphere dry box with the electrolysis cell shown in Figure 11. The anode, intermediate and reference electrode compartments were charged with 0.100M tetraethylammonium perchlorate in acetonitrile and the platinum foil anode and the silver reference electrode inserted into their respective compartments. A mixture of $Ru(CO)(Cl)_2(Ph_3P)_3$ (2.0 g, 2.0 mmoles) in 0.100M tetraethylammonium perchlorate acetonitrile solution (200 ml) was placed in the cathode compartment. To this solution excess triphenylphosphine (1.0 g, 3.8 mmoles) was added and the solution was warmed to 45-50°C and stirred vigorously. A potential of -2.30V vs. a silver/0.100M Ag^+ in acetonitrile reference electrode was applied to the platinum foil cathodes resulting in an initial current of 90 mA. Initially the solution was a clear yellow

Fig.10

Infrared spectrum of

$Ru(CO)(Cl)_2(PhMe_2P)_3$

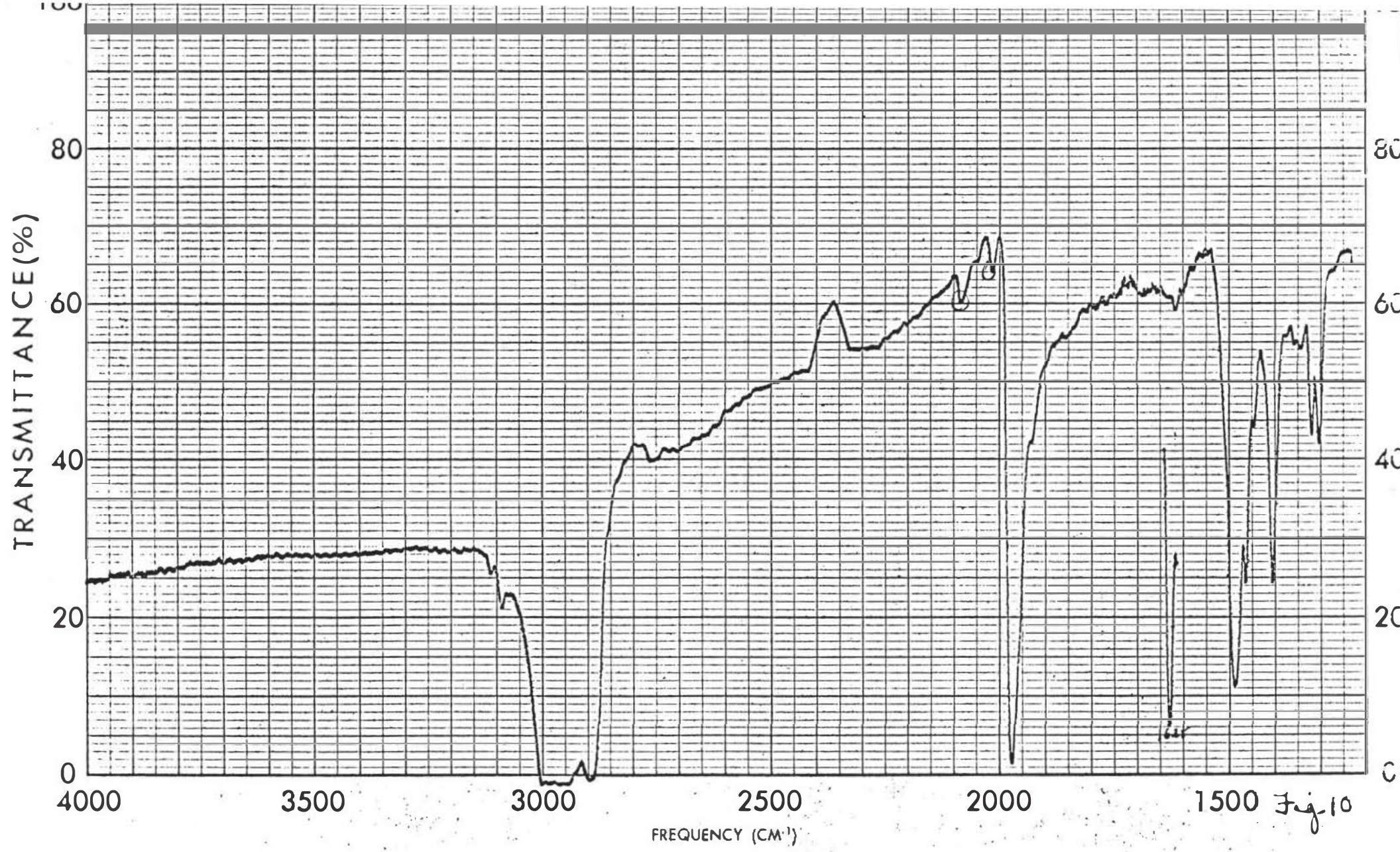
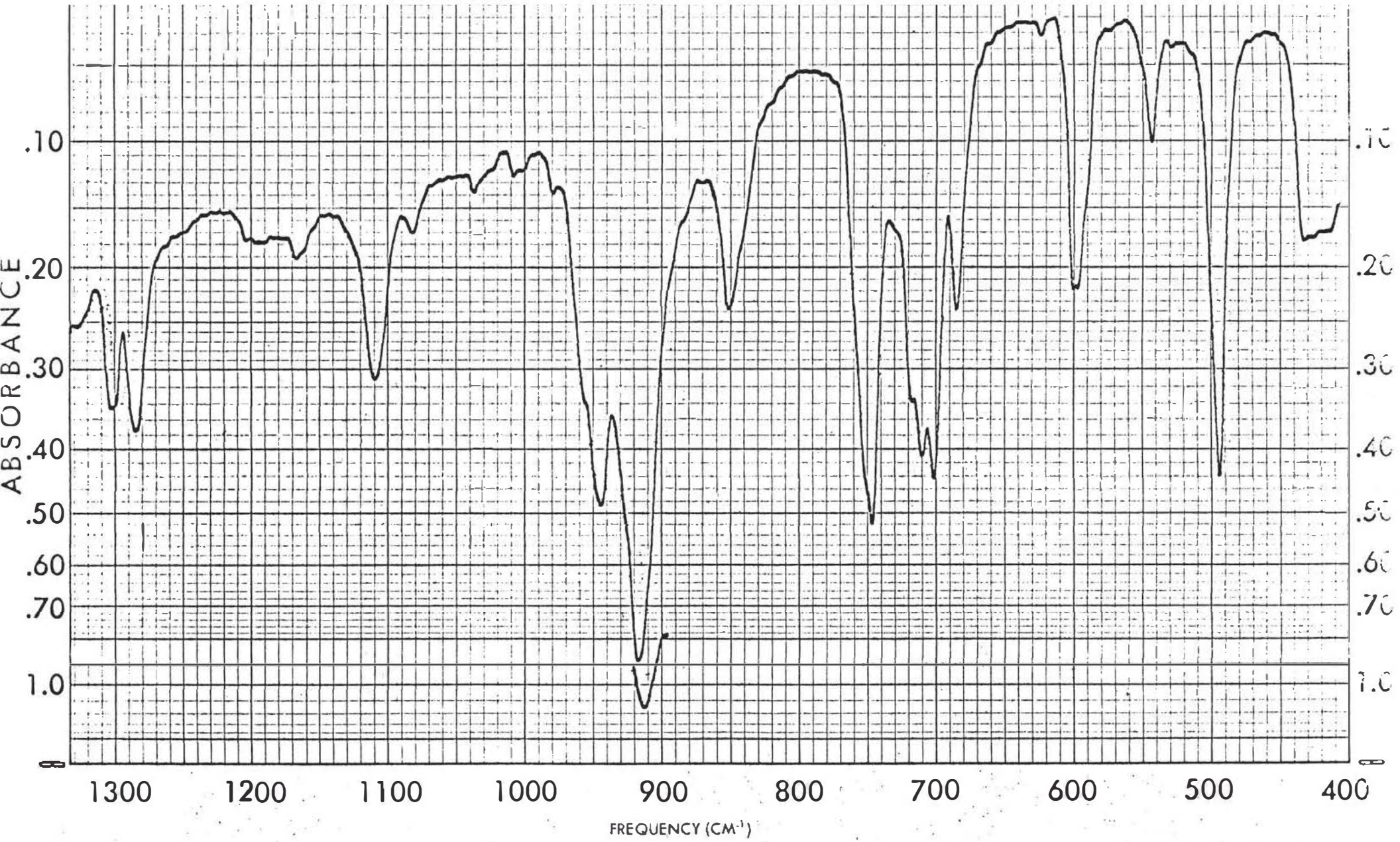


Fig 10

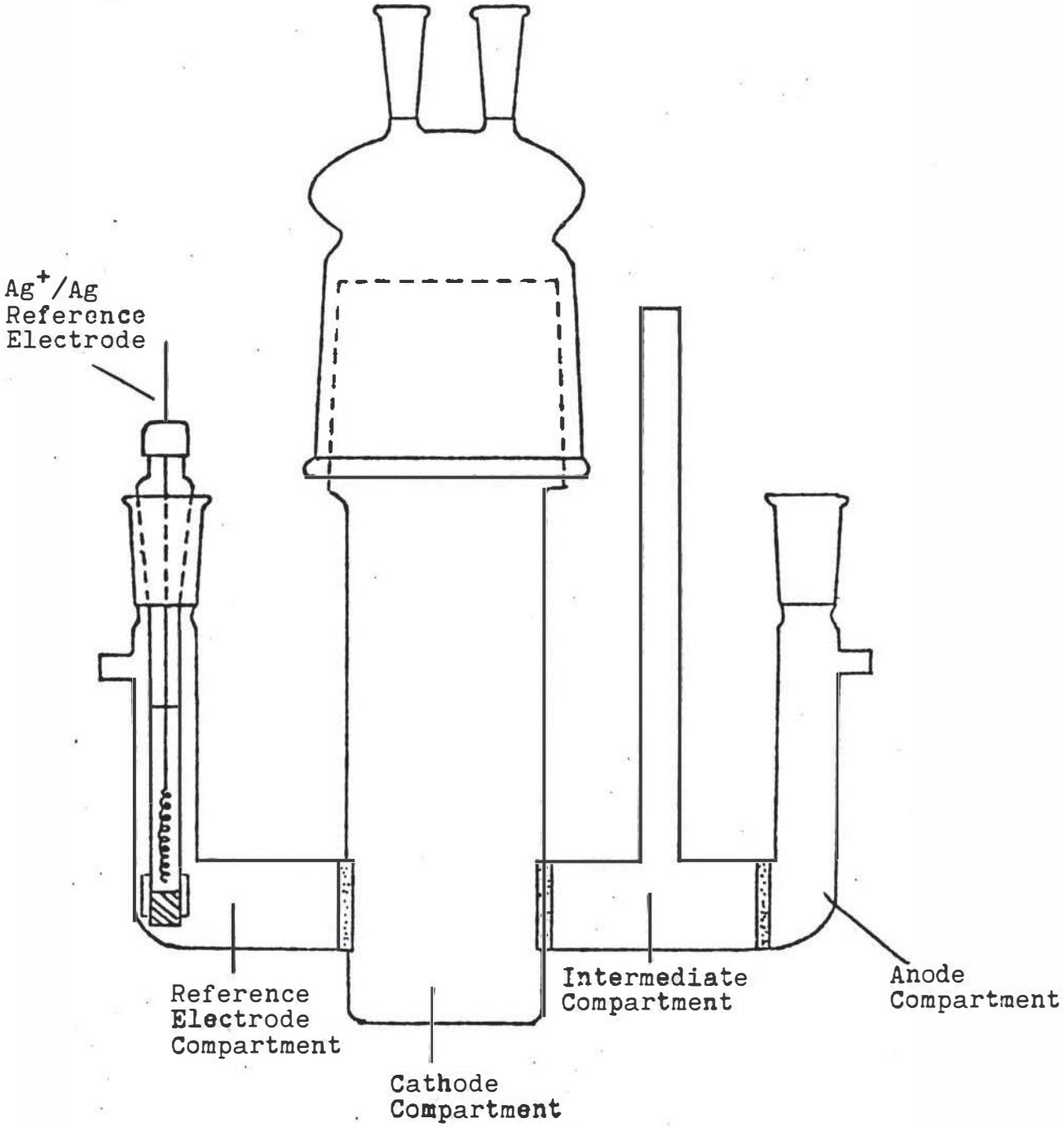
SAMPLE $InCOCl_2(\phi Me_2P)_3$	CURVE NO.	SCAN SPEED Fast	OPERATOR J. Body
	CONC.	SLIT N	DATE 1/29/81
ORIGIN	CELL PATH	REMARKS	
SOLVENT Nujol	REFERENCE		



SAMPLE $RuCoCl_2(pMe_2P)_3$	CURVE NO.	SCAN SPEED	OPERATOR J. Bailey
	CONC.	SLIT	DATE 1/29/81
ORIGIN	CELL PATH	REMARKS	
SOLVENT	REFERENCE		

FIGURE 11

ELECTROLYTIC CELL



color but seconds later as the electrolysis proceeded, the bulk of the catholyte darkened to a deep brick-red color. As the reduction proceeded the solution became opaque due to the formation of red compound. The platinum foil cathodes must be kept free from precipitate during the electrolysis to keep the current from prematurely dropping. After 7 hours, the current had decayed exponentially to 3.6 mA indicating the completion of the reduction. The precipitate is red in color with a deep orange-red supernatant solution. The catholyte was emptied into a 400 ml beaker and a small amount of red solid was removed from the working electrodes surfaces. The solid was filtered and washed with acetonitrile. After drying the solid for 12 hours under vacuum (10^{-2} mm Hg) at 60°C, the yield was determined to be 1.55 g (80%). The solid was stored in the dry box since it was susceptible to decomposition in air. The red compound melted at 177-178°C to a red-brown liquid. Lit: 179-180°C. Characteristic infrared vibration (Fig.12) were observed at 2265 cm^{-1}, $\nu(C\equiv N)$ and 1866, $\nu(C\equiv O)$. (Literature: 2264 cm^{-1}, $\nu(C\equiv N)$; 1865 cm^{-1}, $\nu(C\equiv O)$).

5. Attempted preparations of compounds

a) Ruthenium (II) complexes

(1) Tri-μ-chlorohexakis(triethylphosphine) diruthenium (II) chloride, $(Ru_2Cl_3((C_2H_5)_3P)_6)Cl$.

The procedure for the attempted synthesis of this compound was taken from the work of Chatt and Hayter (6). To a sample of $RuCl_3$ (1.60 g, 7.71 mmoles), 49.6 ml of H_2O was

Fig.12

Infrared spectrum of

$Ru(CO)(CH_3CN)(Ph_3P)_3$

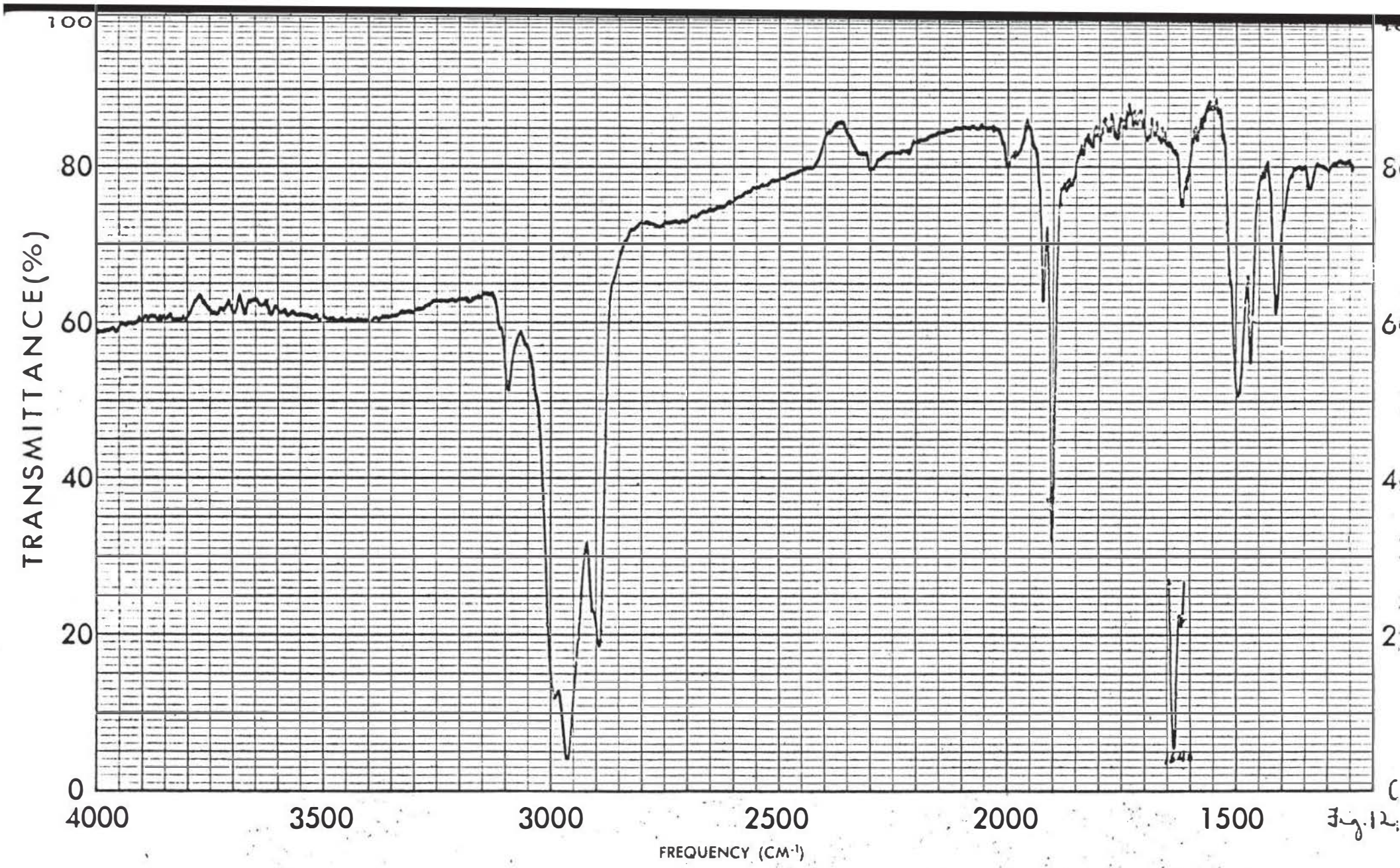
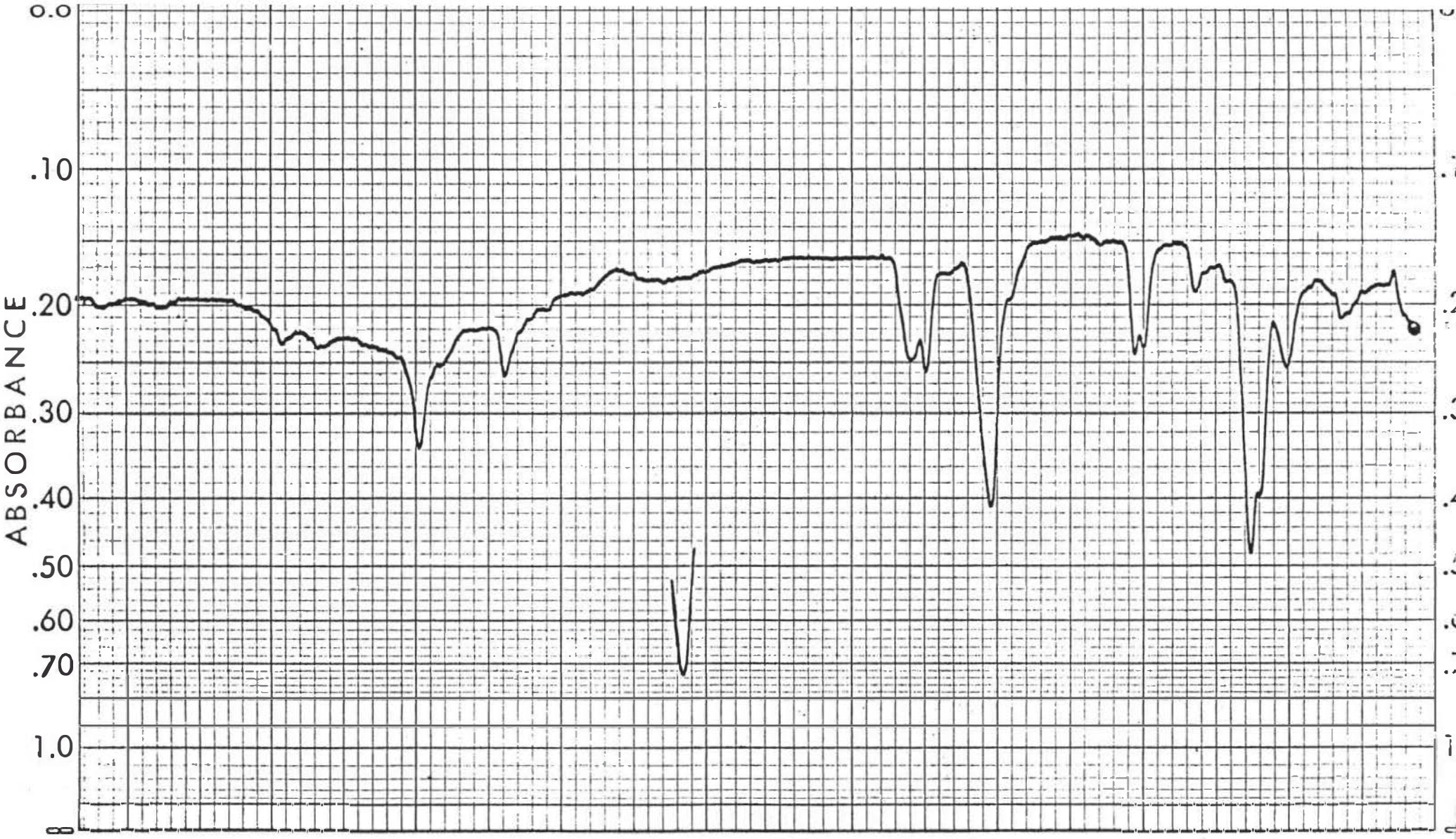


Fig. 12

SAMPLE $(PPh_3)_3RuCO\,CH_3CN$	CURVE NO.	SCAN SPEED	OPERATOR
	CONC.	SLIT	DATE 4/10/81
ORIGIN	CELL PATH	REMARKS	
SOLVENT Nujol	REFERENCE		



SAMPLE $(PPh_3)_3RuClCH_3CN$	CURVE NO.	SCAN SPEED	OPERATOR
	CONC.	SLIT	DATE 4/10/81
ORIGIN	CELL PATH	REMARKS	
GIVEN	REFERENCE		

added. To the resulting solution triethylphosphine (6.54 ml, 5.23 g, 44.2 mmoles) and 149 ml of methanol were added and the mixture was refluxed under nitrogen for 24 hours. The initial solution color was plum purple and remained that color for 24 hours with no sign of precipitate formation. The reaction was continued for another 24 hours with the solution turning dark brown but again no crystals were formed.

(2) Chlorocarbonylhydridotris(diphenylmethylphosphine) ruthenium (II), $Ru(H)(Cl)(CO)((C_6H_5)_2CH_3P)_3$.

The method of Chatt, Shaw and Field (7) was extended in attempting to make this complex. A 0.67 g (0.43 mmoles) sample of $(Ru_2Cl_3(Ph_2CH_3P)_6)Cl$ was dissolved in boiling ethanol (25 ml). Aqueous 1M KOH solution (2 ml) was added and the resultant solution was refluxed for $3\frac{1}{4}$ hours under nitrogen. The solution was cooled and the solvent was removed under vacuum (10^{-3} mm Hg). The resulting residue was extracted with about 35 ml of ether and 100 ml of methanol was added to the ether solution but no crystals formed. Repeated attempts to recrystallize the small amount of ether soluble material failed.

(3) Dichlorocarbonyltris(phenyldimethylphosphine) ruthenium (II), $Ru(CO)(Cl)_2(C_6H_5(CH_3)_2P)_3$.

This method was an attempted extension of the work by Chatt, Shaw and Field (7). In the procedure, $(Ru_2Cl_3(C_6H_5(CH_3)_2P)_6)Cl$

(0.66 g, 0.56 mmoles) was refluxed with boiling ethanol (20 ml) and 2 ml of 1M KOH for 45 minutes under nitrogen. After refluxing, the solution was cooled for 5 minutes and 5 ml of concentrated HCl was added to the solution. No effervescence accompanied the acid addition, but a light tan precipitate formed. The solid was filtered, washed with ethanol and then recrystallized from ethanol. The resulting solid was a white powder with a yield of 0.127 g. In an attempt to isolate more product the remaining supernatant solution was reduced in volume under vacuum yielding a yellow powder. The infrared spectrum of this yellow solid was identical to the chloro-bridged starting material.

An infrared spectrum of the white recrystallized material exhibited no band in the carbonyl region and no characteristic phosphine bands in the fingerprint region. The solid did not melt up to a temperature of 300°C. The reaction was repeated using a reaction time of 24 hours with identical results.

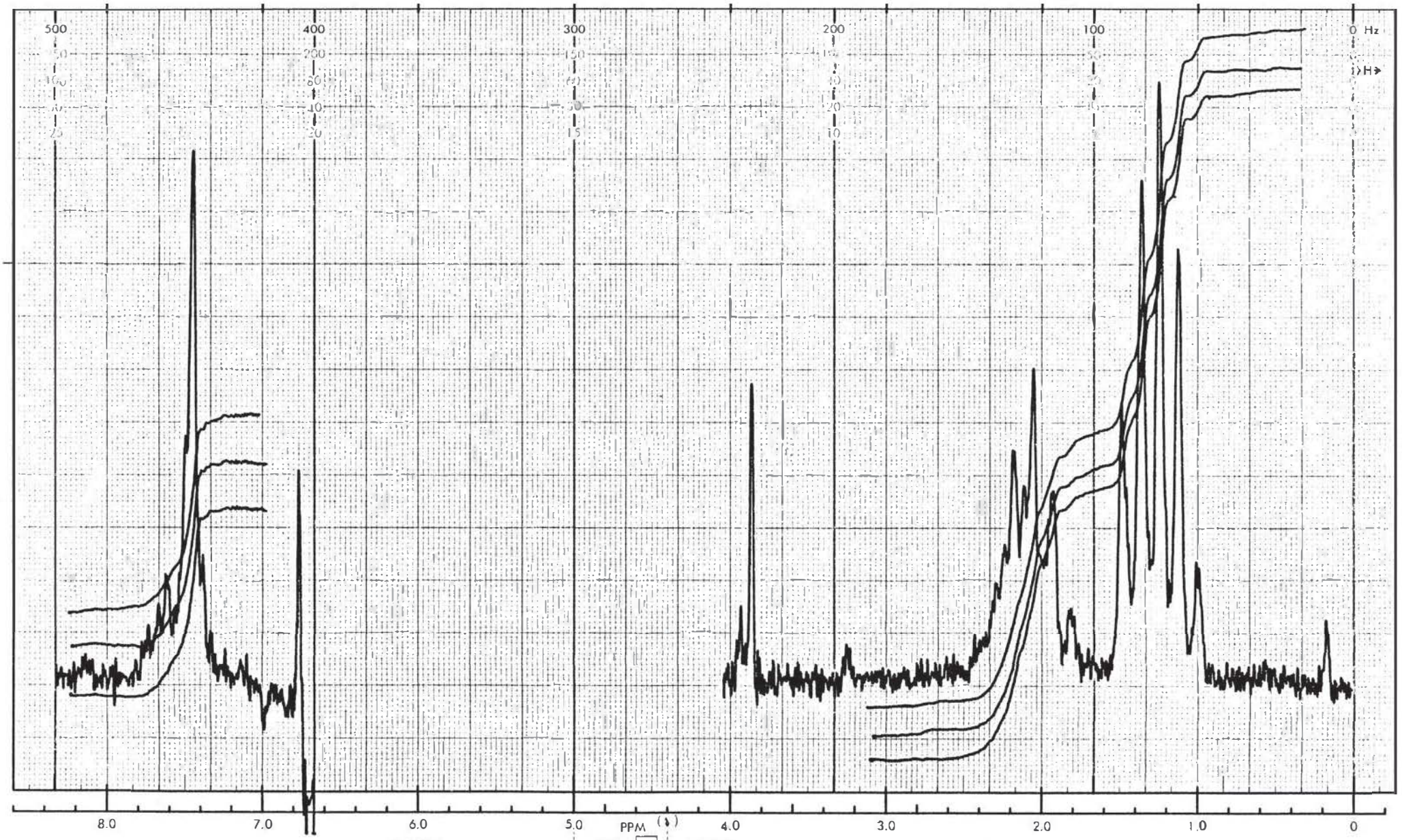
(4) Dichlorocarbonyltris(triethylphosphine) ruthenium (II), $Ru(CO)(Cl)_2((C_2H_5)_3P)_3$.

The synthesis of this complex was tried using a variation of a procedure described by Armit and Stephenson (8). A 1.00 g (1.01 mmoles) sample of $Ru(CO)(Cl)_2(Ph_3P)_3$ was refluxed under nitrogen with triethylphosphine (0.726 ml, 0.581 g, 14.6 mmoles) in 50 ml of degassed hexane for 24 hours. The solid in the suspension changed from bright yellow to pale yellow and diminished markedly in amount. Upon cooling an oil formed in the reaction mixture. The mixture was heated and refluxed for

an additional 24 hours to ensure complete reaction. Cooling again yielded an oil. The supernatant solution was decanted from the oil. Thin layer chromatography on silica gel with CH_2Cl_2 as eluent showed the presence of triphenylphosphine, triethylphosphine and two compounds as components of the oil. The oil was chromatographed on 60-200 mesh silica gel (W. R. Grace Co., 950-08-08) in a 1 cm×15 cm column. With methylene chloride as eluent two fractions containing triphenylphosphine and triethylphosphine were obtained. These components were identified by thin layer chromatography. Final elution with methanol yielded a bright yellow colored fraction. This yellow fraction was reduced to dryness under vacuum (10^{-2} mm Hg) and produced a gummy yellow solid. Upon standing for a day the solid became less gummy. An ^1H nmr of this solid (Fig.13) exhibited a strong peak at 7.5 ppm indicative of triphenylphosphine as well as complex multiplets centered at approximately 2.2 ppm and 1.3 ppm characteristic of the methylene and methyl protons of triethylphosphine, respectively. The relative areas of the observed resonances are in the ratio of 1:1.4:2.1 for phenyl:methylene:methyl protons. Also the relative areas for the phenyl to ethyl protons are 1:3.5, respectively. The solid was washed throughly with hot hexane to ensure the absence of free triethyl- or triphenylphosphine and redried. The ^1H nmr spectrum of the hexane washed solid was identical to that in Figure 13. Thus, the product appears to be a mixture of mixed phosphine complexes. Further attempts to separate this mixture failed.

Fig.13

^{1}H nmr spectrum of products from reaction of $Ru(CO)(Cl)_2(Ph_3P)_3$ with Et_3P



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SPECTRUM AMPLITUDE: 100
INTEGRAL AMPLITUDE: 5
SPINNING RATE (RPS): 4-2

MANUAL
SWEEP TIME (SEC): 50 | 25 | X
SWEEP WIDTH (Hz): 25 | 50 | 100 | 250 | 500 | X
FILTER: 1 | X | 3 | 4 | 5 | 6 | 7 | 8
RF POWER LEVEL: .03

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE: $Ru(CO)Cl_2(\phi_3P)_3$ in et_3P

SOLVENT: CH_2Cl_2

REMARKS: Lock on CH_2Cl_2

Fig. 13

DATE: 5/7/81

OPERATOR: J. Bady

60 MHz NMR
SPECTRUM NO.

GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK
PRINTED IN U.S.A.
No. VN 1009 (S-60T)

b) Ruthenium (0) complexes

(1) Acetonitrilecarbonyltris(diphenylmethylphosphine) ruthenium (0), $Ru(CO)(CH_3CN)((C_6H_5)_2CH_3P)_3$

The attempted synthesis of this compound was done on both a small scale as well as a larger scale. On the small scale, diphenylmethylphosphine (0.0968 ml, 0.515 mmoles) and $Ru(CO)(CH_3CN)(Ph_3P)_3$ (0.150 g, 0.157 mmoles) was warmed with stirring in 10 ml of CH_3CN. The temperature was kept in the range 30-31°C. The solution was stirred for 27 hours with the color of the solution turning from dark orange to light yellow. A fine yellow powder formed in the flask. The powder was filtered and washed with CH_3CN, but only a tiny amount (<1 mg) was obtained.

On the larger scale, 1.00 g (1.04 mmoles) of $Ru(CO)(CH_3CN)(Ph_3P)_3$ and Ph_2MeP (0.600 ml, 3.18 mmoles) was heated in 50 ml of CH_3CN. The temperature of the solution was kept at 50-52°C. After heating overnight (12 hours) there was no observable color change from the initial orange-red color. Also an appreciable amount of the starting material had not dissolved. An additional 0.2 ml (1.06 mmoles) of Ph_2MeP ligand was added to the solution. Five minutes after adding the ligand, all of the solid dissolved and the solution changed from orange-red to wine-red. After four hours the color had turned a yellowish-orange and was slightly cloudy. The solution was filtered and a trace amount of black solid was removed. The remaining solution was a clear golden orange. This golden orange solution's volume

was reduced under vacuum (10^{-3} mm Hg) to form a yellow oil. The oil was triturated with about 25 ml of degassed hexane at reflux with constant stirring for 24 hours. A light tan powder formed which was removed by filtration, washed with hexane and dried at 50°C under vacuum (10^{-2} mm Hg). The amount of isolated solid was 0.254 g. This solid melted with decomposition at 120-122°C. The infrared spectrum (Fig.14) exhibited a band at 1920 cm^{-1} which was tentatively assigned to a carbonyl stretching mode. A broad medium intensity peak at 2155 cm^{-1} which could possibly arise from hydrido- and/or acetonitrile ligand was observed . The infrared spectrum also showed bands at 1540-1550 and 730 cm^{-1} which are indicative of ortho-metallation at a phenyl ring of the ligand. The ^1H nmr spectrum (Fig.15) exhibited a broad peak at 7.0-7.1 ppm that was attributed to phenyl protons. From 0.7 to 2.0 ppm, there appeared a poorly resolved complex pattern. A ^1H nmr spectra taken upfield from TMS showed no signal characteristic of a hydrido ligand. The values from the elemental analysis of the material fit no simple formulation. Calculated for $Ru(CO)(CH_3CN)(Ph_2MeP)_3$: C,65.45; H,5.49; P,12.06%. Found: C,63.34; H,6.22; P,8.97%. From the collected information it was concluded that $Ru(CO)(CH_3CN)(Ph_2MeP)_3$ was not made but the product is much more complex and is most probably a mixture.

(2) Acetonitrilecarbonyltris(dimethylphenylphosphine) ruthenium (0), $Ru(CO)(CH_3CN)(C_6H_5(CH_3)_2P)_3$.

In attempting to synthesize this complex, dimethylphenyl-

Fig.14

Infrared spectrum of isolated solid from reaction of $Ru(CO)(CH_3CN)(Ph_3P)_3$ with Ph_2MeP

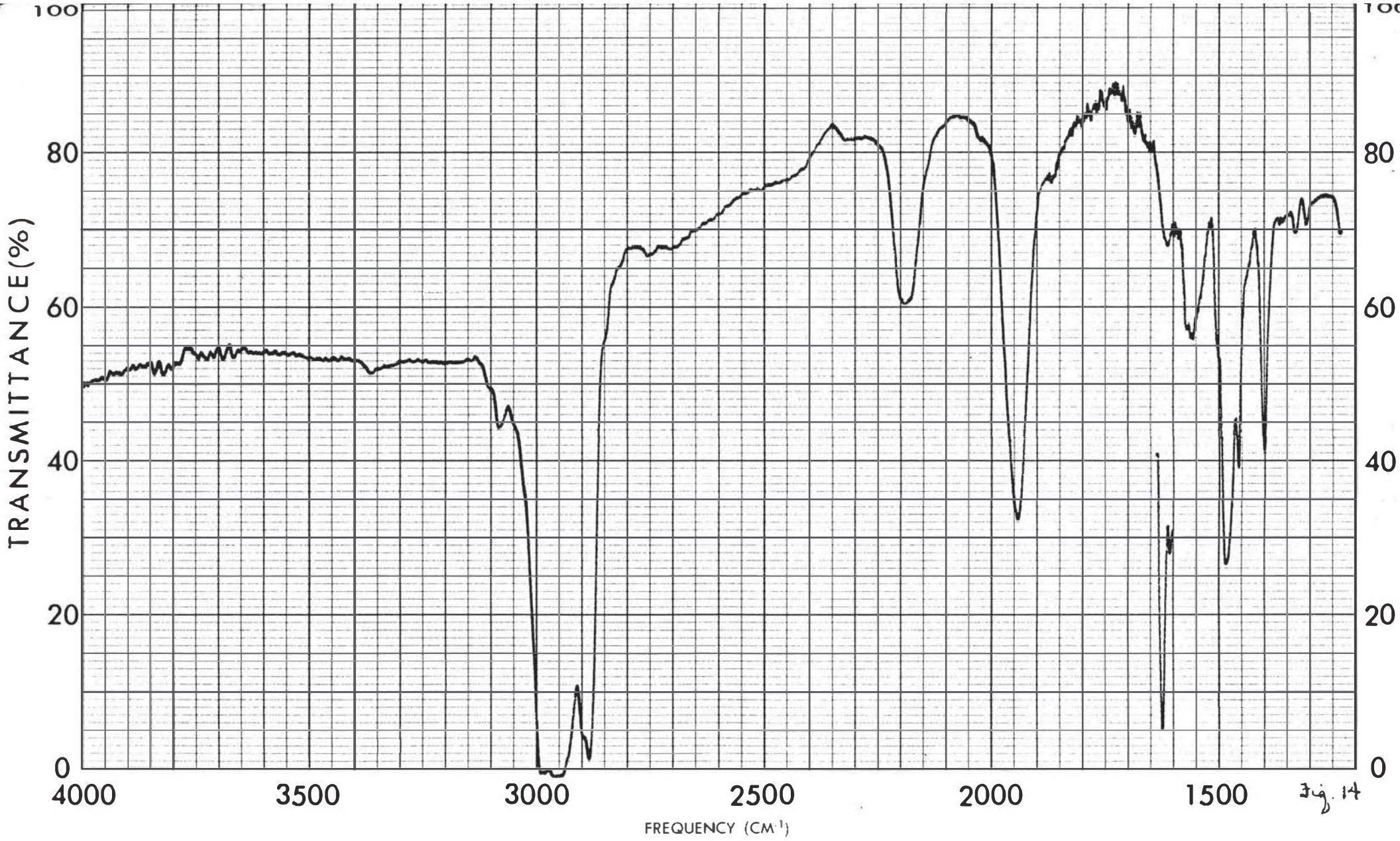
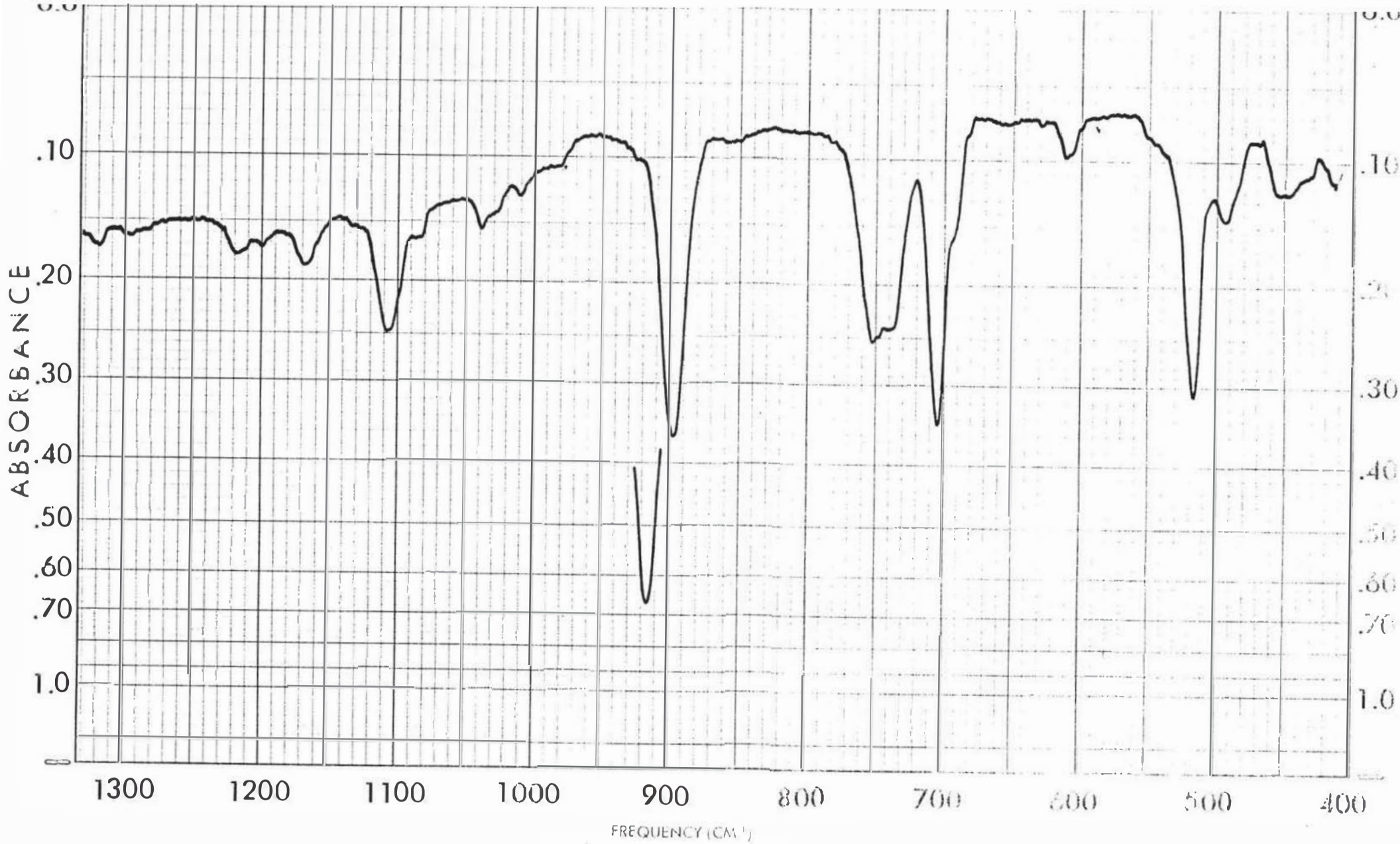


Fig. 14

SAMPLE $Ru(CO)(CH_3CN)(\phi_2MeP)_3$ (?)	CURVE NO.	SCAN SPEED 7	OPERATOR Badri
	CONC.	SLIT N	DATE 4/22/81
ORIGIN	CELL PATH	REMARKS tan powder	
SOLVENT Nujol	REFERENCE		

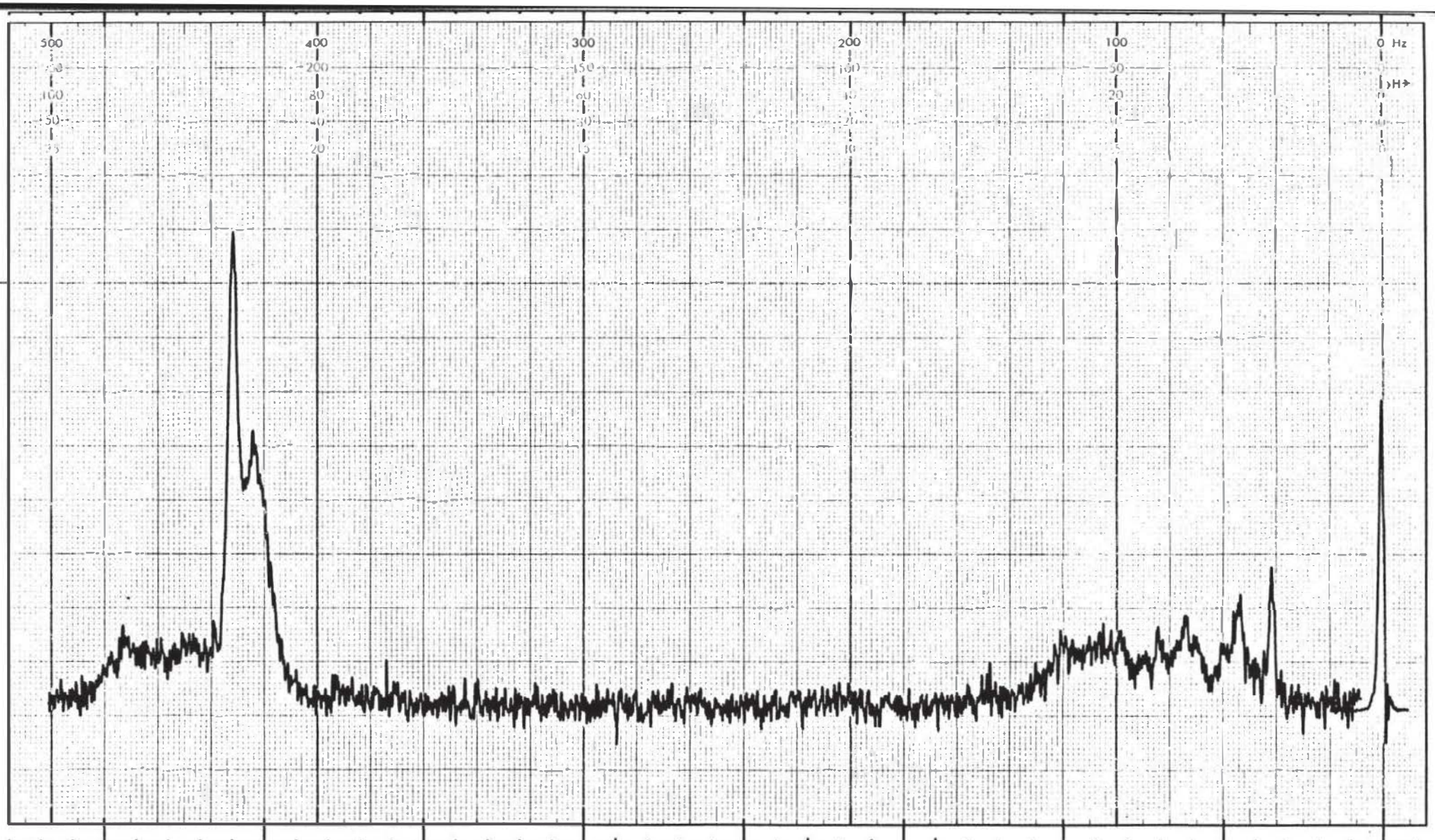


SAMPLE $Ru(CO)(CH_3CN)(\phi_2MeP)_3$	CURVE NO.	SCAN SPEED	OPERATOR
	CONC.	SLIT	DATE 4/22/81
ORIGIN	CELL PATH	REMARKS tan powder	
SOLVENT	REFERENCE		

Fig.15

^1H nmr spectrum of solid isolated

from reaction of $Ru(CO)(CH_3CN)(Ph_3P)_3$ with Ph_2MeP



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SPECTRUM AMPLITUDE: 125
INTEGRAL AMPLITUDE:
SPINNING RATE (RPS): 40

MANUAL
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SWEEP WIDTH (Hz): 25 50 100 250 [X]
FILTER: 1 [X] 3 4 5 6 7 8
RF POWER LEVEL: .03

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE: $RuCl_2(CH_3CN)(C\phi_3P)_3$ in ϕ_2MeP

REMARKS: Fig. 15

SOLVENT: d-benzene

DATE: 5/7/81

OPERATOR: J. Bady

60 MHz NMR
SPECTRUM NO.

RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK
PRINTED IN U.S.A.
No. VN 1009 (S-60T)

phosphine (0.0739 ml, 0.517 mmoles) and $Ru(CO)(CH_3CN)(Ph_3P)_3$ (0.150 g, 0.157 mmoles) was heated with stirring in 10 ml of CH_3CN for 24 hours. The solution changed from orange-red to light yellow and a beige powder formed. This powder was filtered off and washed with acetonitrile. The powder was dried under vacuum (10^{-2} mm Hg) for 12 hours. Less than 3 mg were collected. With so little product isolated, the supernatant liquid was reduced under vacuum (10^{-3} mm Hg). A yellow-brown oil formed. No crystalline product could be obtained from this oil using a variety of solvent mixtures including benzene/hexane, toluene/hexane, and toluene/ligroin. A melting point was taken of the powder that was collected. The solid melted at 140-142°C (d).

(3) Acetonitrilecarbonyltris(triethylphosphine) ruthenium (0), $Ru(CO)(CH_3CN)((C_2H_5)_3P)_3$.

A ligand exchange reaction between $Ru(CO)(CH_3CN)(Ph_3P)_3$ and triethylphosphine was attempted. Triethylphosphine (0.0765 ml, 0.518 mmoles) and $Ru(CO)(CH_3CN)(Ph_3P)_3$ (0.150 g, 0.157 mmoles) were refluxed and stirred in 10 ml of CH_3CN for 24 hours. When the Et_3P was injected into the complex containing solution there was an almost immediate color change from orange-red to yellow. A beige powder separated from the solution during the reaction. The powder was filtered, washed with CH_3CN and dried under vacuum (10^{-2} mm Hg) for 24 hours. The powder weighed 4.9 mg. The supernatant liquid was evaporated under vacuum and a yellow oil formed. The yellow oil could not be crystallized using various toluene/

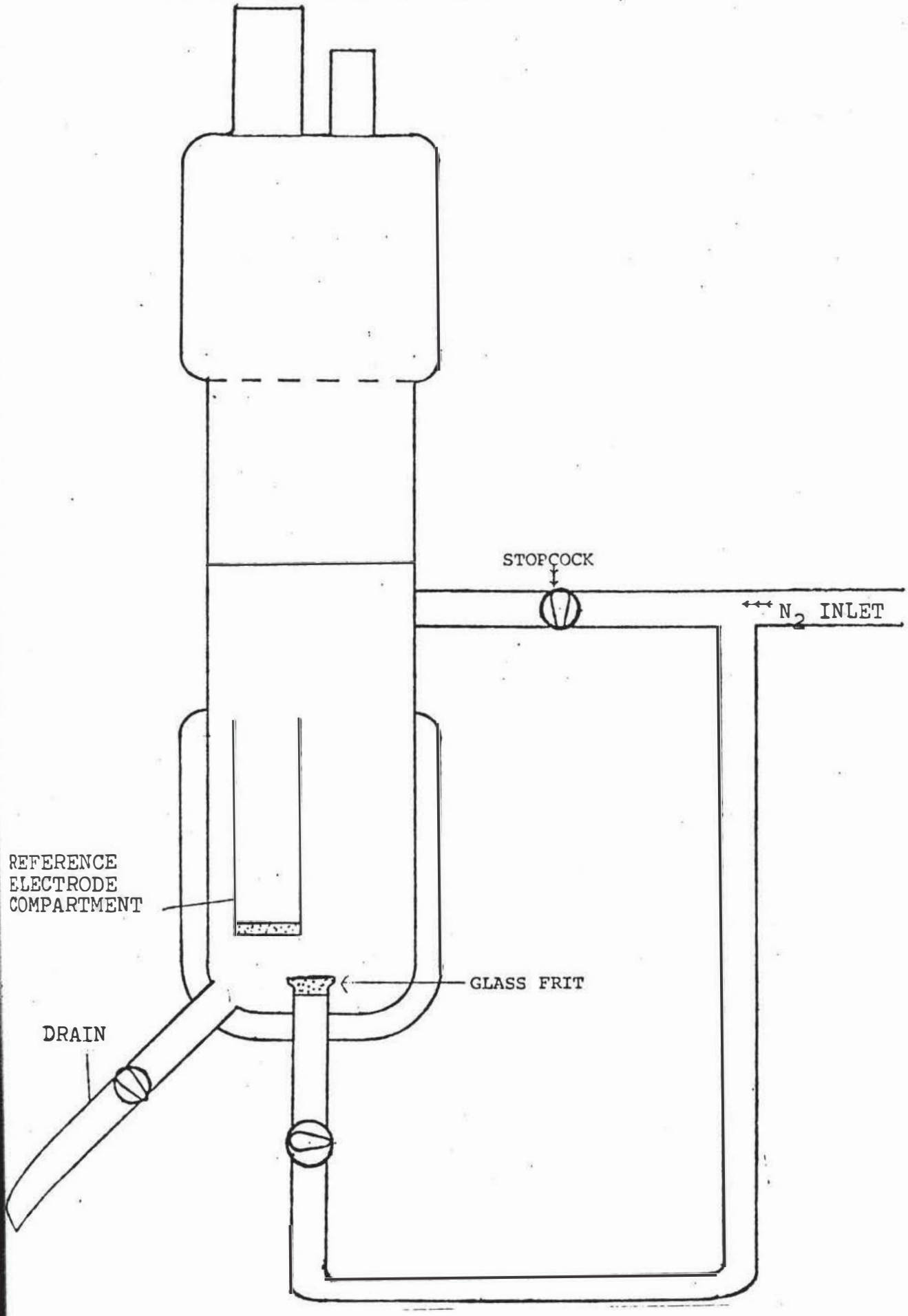
heptane mixtures and cooling to -15°C. The melting point of the powder that was obtained had a range of 140-142°C (decomposed). It appears that the beige powder obtained was similar to that also isolated in the ligand exchange reactions and the principal products were oils which could not be crystallized.

6. Polarography and Voltammetry of $Ru(CO)(Cl)_2((C_6H_5)_2CH_3P)_3$ and $Ru(CO)(Cl)_2(C_6H_5(CH_3)_2P)_3$.

In determining the redox behavior of these complexes, 1.00×10^{-3}M solutions (50.0 ml), in acetonitrile, containing 0.100M tetraethylammonium perchlorate were made. The solution of each complex was prepared in the dry box. The solution was transferred from the dry box using a 50 ml syringe and injected into the electrolytic cell which had been throughly purged with nitrogen. The electroanalytical cell is shown in Figure 16. The dropping mercury electrode, the reference electrode compartment, the reference electrode and a platinum wire auxillary electrode were then inserted into the test solution. The details of the Ag^+/0.100M $AgNO_3$ in acetonitrile reference electrode are shown in Figure 17. The test solution was degassed thoroughly with nitrogen prior to the polarographic measurements.

Voltammetric measurements were performed on the same solution used for polarography. A spherical platinum microelectrode was used instead of the dropping mercury electrode. The solution at the electrode surface was stirred briefly with a stream of nitrogen before each voltammogram to remove any products produced during

FIGURE 16. POLAROGRAPHIC AND VOLTAMMETRIC CELL

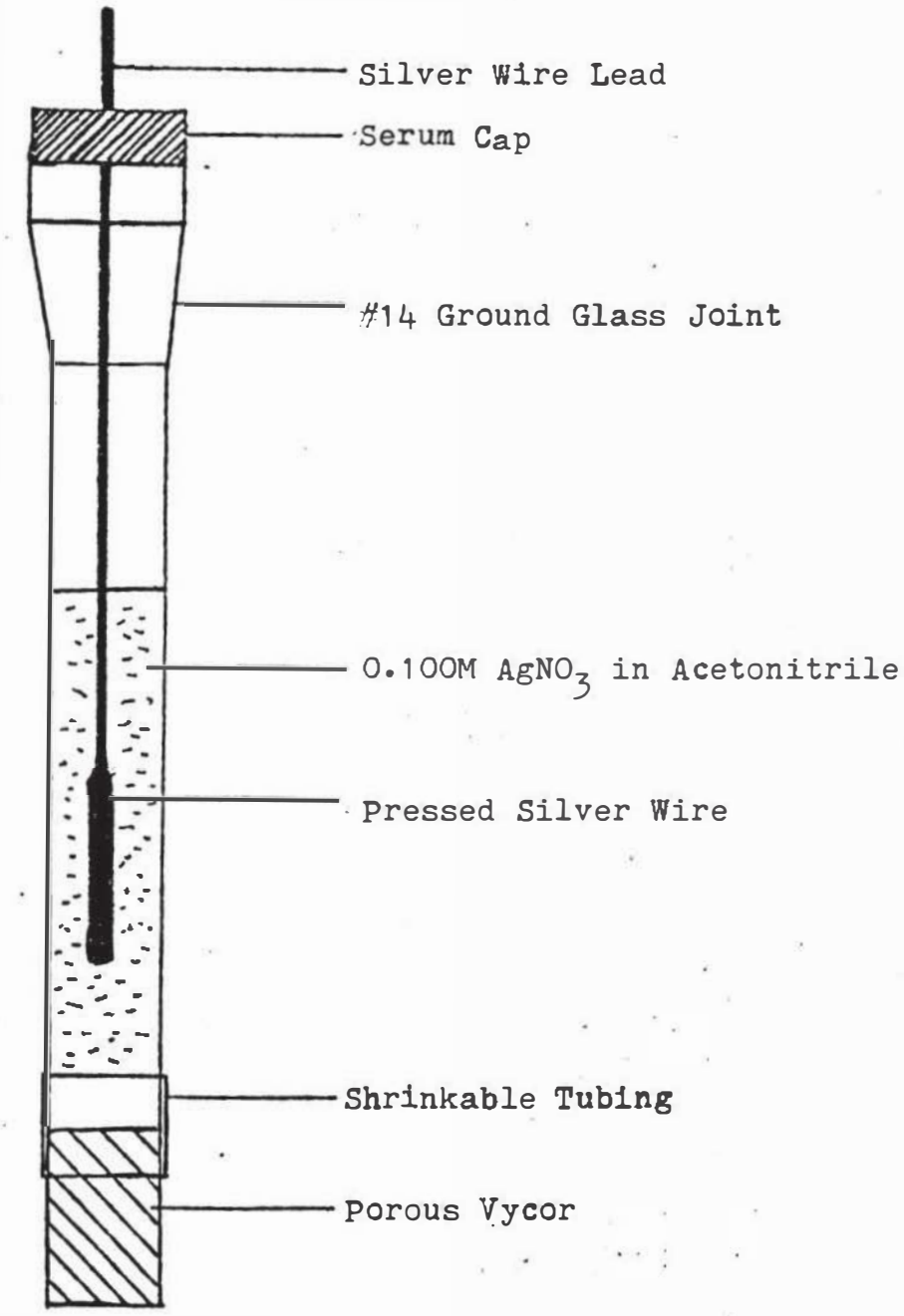


previous voltage sweeps from the interface.

The test solutions were kept under a nitrogen atmosphere during all electrochemical measurements.

FIGURE 17

Ag/.1M $AgNO_3$ in Acetonitrile Reference Electrode



Results and Discussion

A. Synthesis of Ruthenium (II) complexes

1. Synthesis of dichlorocarbonyltris(triphenylphosphine) ruthenium (II), $Ru(CO)(Cl)_2((C_6H_5)_3P)_3$.

The compound, dichlorocarbonyltris(triphenylphosphine) ruthenium (II), was synthesized by the following series of reactions.

$$RuCl_3 + 3Ph_3P \xrightarrow{CH_3OCH_2CH_2OH} Ru(H)(CO)(Cl)(Ph_3P)_3$$

$$Ru(H)(CO)(Cl)(Ph_3P)_3 + HCl \xrightleftharpoons{CH_2Cl_2} Ru(CO)(Cl)_2(Ph_3P)_3 + H_2$$

The isolated product from these reactions was identified by its elemental analysis and the presence of the carbonyl ligand confirmed by the strong carbonyl stretching frequency at 1955 cm^{-1} observed in the infrared spectrum.

Olson (1) has carried out the same set of reactions and reports the isolation of a μ-dichloro bridged ruthenium dimer, $(Ru(CO)(Cl)_2((C_6H_5)_3P)_2)_2$. The dimeric product was obtained by crystallization at low temperature from the mother liquor from the second reaction after partial removal of the CH_2Cl_2 solvent under vacuum. The product, $Ru(CO)(Cl)_2(Ph_3P)_3$, on the other hand, was isolated by total removal of the methylene chloride from the mother liquor of the second reaction. These two isolated materials are different as shown by comparison of their physical properties and elemental analyses (Table 1).

Table 1

Comparison of Physical Properties and Elemental Analyses for $Ru(CO)(Cl)_2(Ph_3P)_3$ and $(Ru(CO)(Cl)_2(Ph_3P)_2)_2$

	$Ru(CO)(Cl)_2(Ph_3P)_3$	$(Ru(CO)(Cl)_2(Ph_3P)_2)_2$
color	orange-yellow	bright yellow
melting point, °C	210-215	215-220
%C	66.74	61.33
%H	4.60	4.17
%P	9.61	8.56

It is proposed that the isolation of these two materials from a common reaction sequence arises from a equilibrium in CH_2Cl_2 between the monomeric ruthenium complex, a coordinatively unsaturated intermediate and the chlorobridged dimer as shown in the scheme below.

$$Ru(CO)(Cl)_2(Ph_3P)_3 \rightleftharpoons (Ru(CO)(Cl)_2(Ph_3P)_2) + Ph_3P$$

$$\downarrow$$

$$\tfrac{1}{2}(Ru(CO)(Cl)_2(Ph_3P)_2)_2$$

The suggested coordinatively unsaturated intermediate, $(Ru(CO)(Cl)_2(Ph_3P)_2)$, has not been detected or isolated. In the preparative procedure used in this work, as the solvent is removed the equilibrium involving the dissociative loss of triphenylphosphine from the tris-coordinated phosphine monomer would be shifted to the left thereby favoring the monomer.

A coordinatively unsaturated compound of the same empirical formula as that postulated here has been invoked by Olson (1) to explain the low molecular weights observed for

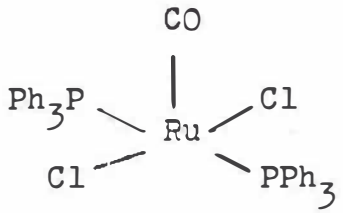
$(Ru(CO)(Cl)_2(Ph_3P)_2)_2$ in chlorinated solvents. The observed molecular weights were half of that expected for the dimer and a dissociative equilibrium in such solvents was suggested.

$$(Ru(CO)(Cl)_2(Ph_3P)_2)_2 \rightleftharpoons 2Ru(CO)(Cl)_2(Ph_3P)_2$$

Dissociation of the dimer was also accompanied by a shift in the carbonyl stretching frequency from 1975 to 1964 cm^{-1} for the dimer and the monomer, respectively. Spectroscopic studies of chloroform solutions of the dimer upon the addition of σ-donor ligands such as acetonitrile or pyridine indicated the formation in solution of six coordinate ruthenium complexes with these ligands, but these materials could not be isolated.

$$Ru(CO)(Cl)_2(Ph_3P)_2 + L \rightleftharpoons Ru(CO)(Cl)_2(Ph_3P)_2L$$

The original dimer, however, was recovered after work-up of these chloroform solutions. A square pyramidal structure was proposed for the coordinatively unsaturated dissociation product.



This structure is similar to that observed for the coordinatively unsaturated compound $RuCl_2(Ph_3P)_3$ as shown by La Placa and Ibers(10) and Armit, Boyd and Stephenson (11).

Further evidence that $Ru(CO)(Cl)_2(Ph_3P)_3$ can lead to a di-

meric product was obtained from the behavior of this compound when treated with acetonitrile. When $Ru(CO)(Cl)_2(Ph_3P)_3$ was placed in acetonitrile under nitrogen, the material dissolved with simultaneous precipitation of a greenish-yellow solid. Elemental analysis of this material agreed with an empirical formula, $Ru(CO)(Cl)_2(Ph_3P)_2$. The solid melted at 245-250 °C and was very slightly air sensitive discoloring over a period of several weeks. The very low solubility of this compound in a variety of solvents suggests that it is a dimer. The compound is very slightly soluble in methylene chloride, tetrahydrofuran and benzene and appears insoluble in acetone. Therefore, in acetonitrile the reaction observed is

$$2Ru(CO)(Cl)_2(Ph_3P)_3 \underset{\longleftarrow}{\xrightarrow{CH_3CN}} (Ru(CO)(Cl)_2(Ph_3P)_2)_2 + 2Ph_3P$$

Approximately 76% of the expected amount of Ph_3P for this reaction stoichiometry was recovered. The isolated triphenylphosphine was identified by its melting point and infrared spectrum.

The dimer isolated by reaction of $Ru(CO)(Cl)_2(Ph_3P)_3$ in acetonitrile is different from that reported by Olson on the basis of color, melting point, solubility in chlorinated solvents and frequency of the carbonyl stretching bands as shown in Table 2.

Table 2

Comparison of the Physical Properties of the Dimer of the Formula $(Ru(CO)(Cl)_2(Ph_3P)_2)_2$

Property	Dimer from work of Olson	Dimer from this work
color	bright yellow	greenish yellow
m.p., °C	215-220	245-250
CH_2Cl_2 solubility	readily soluble	very slightly soluble
ν(CO)	1975(s) cm^{-1}	1961(s), 1945(s) cm^{-1}

The observed low solubility of the dimer isolated in this work in benzene suggests that it is a μ-dichlorobridged species rather than a μ- tri-chlorobridged compound as has been reported by Lupin and Shaw (13) for mixed alkylaryl and trialkyl phosphine non-carbonyl containing complexes of ruthenium (II). These μ-trichloro-compounds have the formula, $(Ru_2Cl_3(R_3P)_3)Cl$.

There are twelve possible isomers for a dichlorobridged dimer containing two phosphines, a carbonyl and a chloro ligand on each ruthenium center in addition to the bridging chloro ligands. Four of these isomers would be expected from their symmetry (C_i or C_{2h}) to exhibit a single carbonyl stretching band whereas eight isomers (C_{2s}, C_2 or C_{2v} symmetry) would yield two carbonyl stretching bands. The infrared spectrum for the dimer prepared in this work (Table 2) shows two carbonyl bands but it is impossible to determine the structure with the available data. It should be noted that the dimer prepared by Olson exhibits only a single carbonyl stretching band and, therefore, these two compounds are isomers with different symmetry.

2. Synthesis of dichlorocarbonyltris(diphenylmethylphosphine)ruthenium (II), $Ru(CO)(Cl)_2((C_6H_5)_2(CH_3)P)_3$

For the synthesis of this compound, two methods were utilized. The first attempted procedure was based on the work of Chatt, Shaw and Field (7). The reaction scheme can be represented as a two step process.

$$(Ru_2Cl_3(Ph_2MeP)_6)Cl + 2KOH + 2C_2H_5OH \longrightarrow 2RuHCl(CO)(Ph_2MeP)_3 + 2CH_4 + 2KCl + 2H_2O$$

$$RuHCl(CO)(Ph_2MeP)_3 + HCl \longrightarrow Ru(CO)(Cl)_2(Ph_2MeP)_3 + H_2$$

The yield of the compound isolated by this method was 93%. The melting point range of the solid was 223-225°C yielding a yellow liquid. The second method used was a procedure adapted from the work of Armit and Stephenson (8) on the ligand exchange of noncarbonyl containing ruthenium (II) complexes. The reaction is shown below:

$$Ru(CO)(Cl)_2(Ph_3P)_3 + xsPh_2MeP \xrightarrow{Hexane} Ru(CO)(Cl)_2(Ph_2MeP)_3 + Ph_3P$$

The one step process gave a comparable yield of 90%. Elemental analysis agreed with the required empirical formula. The solid melted at 205°C.

The infrared spectra of the product obtained by each method were almost identical. The material prepared by the Chatt, Shaw and Field method exhibited carbonyl bands at 1938 and

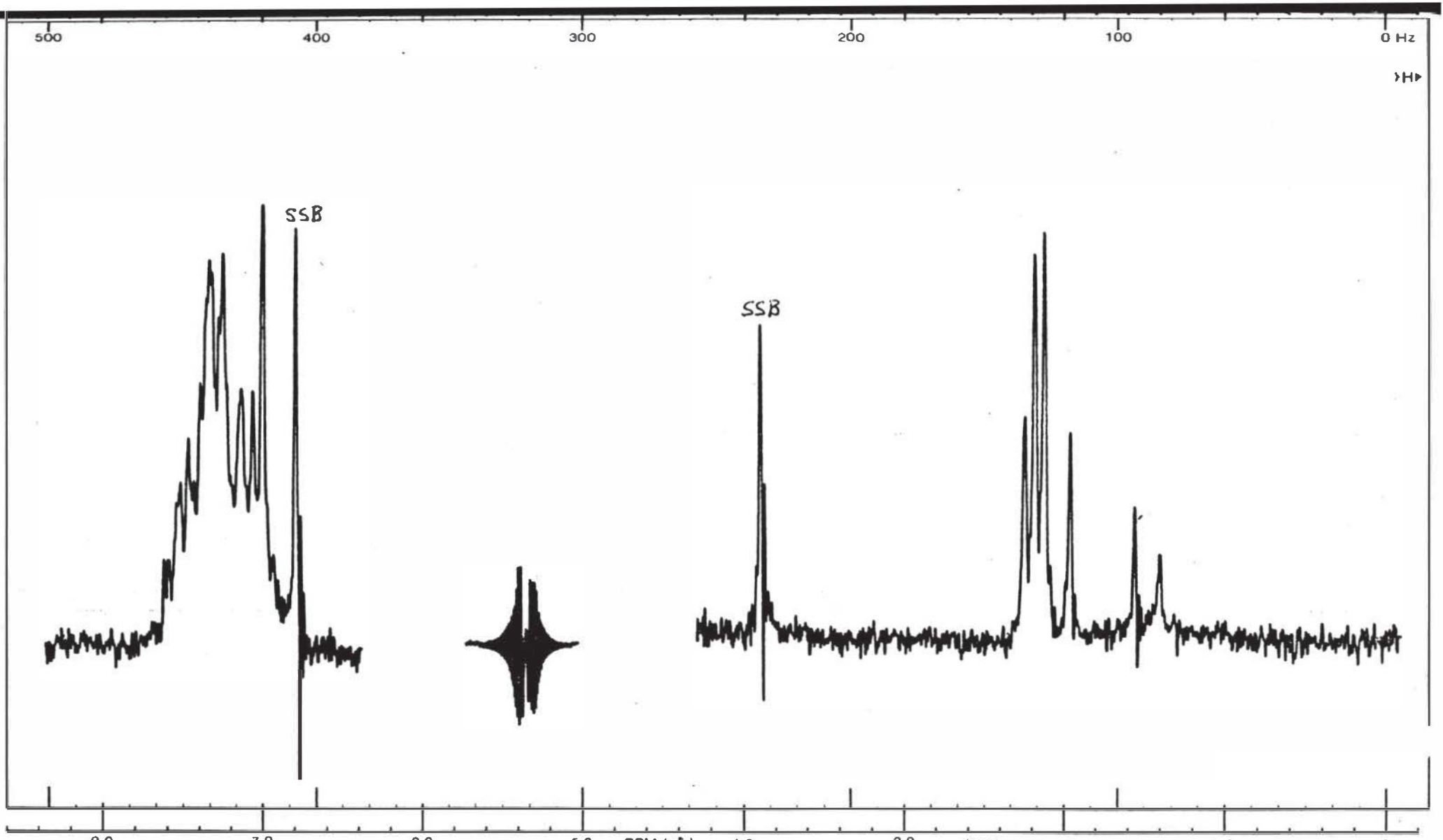
1952 cm^{-1}, and that from the ligand exchange method showed carbonyl bands at 1945 and 1954 cm^{-1}. The infrared spectra of the product from the ligand exchange method also exhibited bands at 2060 and 2000 cm^{-1}. These are probably due to an impurity which arises in the synthesis of the starting material, $Ru(CO)(Cl)_2(Ph_3P)_3$. C. Mooney (12) has since shown that recrystallization of the off-white, crude product from methanol yielded a pure white solid. The infrared spectrum of the white solid showed the absence of these bands at 2060 and 2000 cm^{-1}. The presence of this impurity also explains the lower melting point for the product made by this method.

The ^1H nmr spectra of the products obtained by the independent synthetic methods were identical as shown in Figure 18 and Figure 19. The spectra exhibited an overlapping doublet (δ = 2.08 ppm; J_{PH} = 9.5 Hz) and triplet (δ = 2.23 ppm; J_{PH} = 3.8 Hz). A multiplet was also observed at 7.4 ppm. The triplet and the doublet are attributed to the methyl groups of the phosphine ligands. The triplet at 2.23 ppm is due to virtual coupling of the methyl groups of two mutually trans phosphine ligands and the doublet at 2.08 ppm is assigned to a methyl substituents of a cis phosphine ligand. The multiplet at 7.4 ppm is characteristic of phenyl groups of the phosphine ligands in the compound. The relative intensities of the doublet:triplet is 2:1. The peak shown at 1.6 ppm in both Figure 18 and 19 is an impurity that arises from the solvent, methylene chloride.

A ^{31}P nmr spectrum (Figure 20) was obtained for the complex made by ligand exchange. A doublet (relative area = 2) is

Figure 18

^1H nmr spectrum of $Ru(CO)(Cl)_2(Ph_2MeP)_3$ prepared by method of Chatt, Shaw and Field in CH_2Cl_2



SWEEP OFFSET (Hz): 1000
SPECTRUM AMPLITUDE: 100
INTEGRAL AMPLITUDE: .....
SPINNING RATE (RPS): 45

MANUAL
SWEEP TIME (SEC): 50 250 500 1000
SWEEP WIDTH (Hz): 25 50 100 250 500
FILTER: 1 X 3 4 5 6 7 8
RF POWER LEVEL: 10.3

AUTO ☐
(250)
(500)
(2)
(.05)

SAMPLE: $(\phi_3 P)_3 Ru(Cl)_2 Cl_2$ (1st prep) REMARKS: Lock CH_2Cl_2
SOLVENT: CH_2Cl_2 Lock power ↓
DEC.LEVEL ..... fresh soln

Fig. 18

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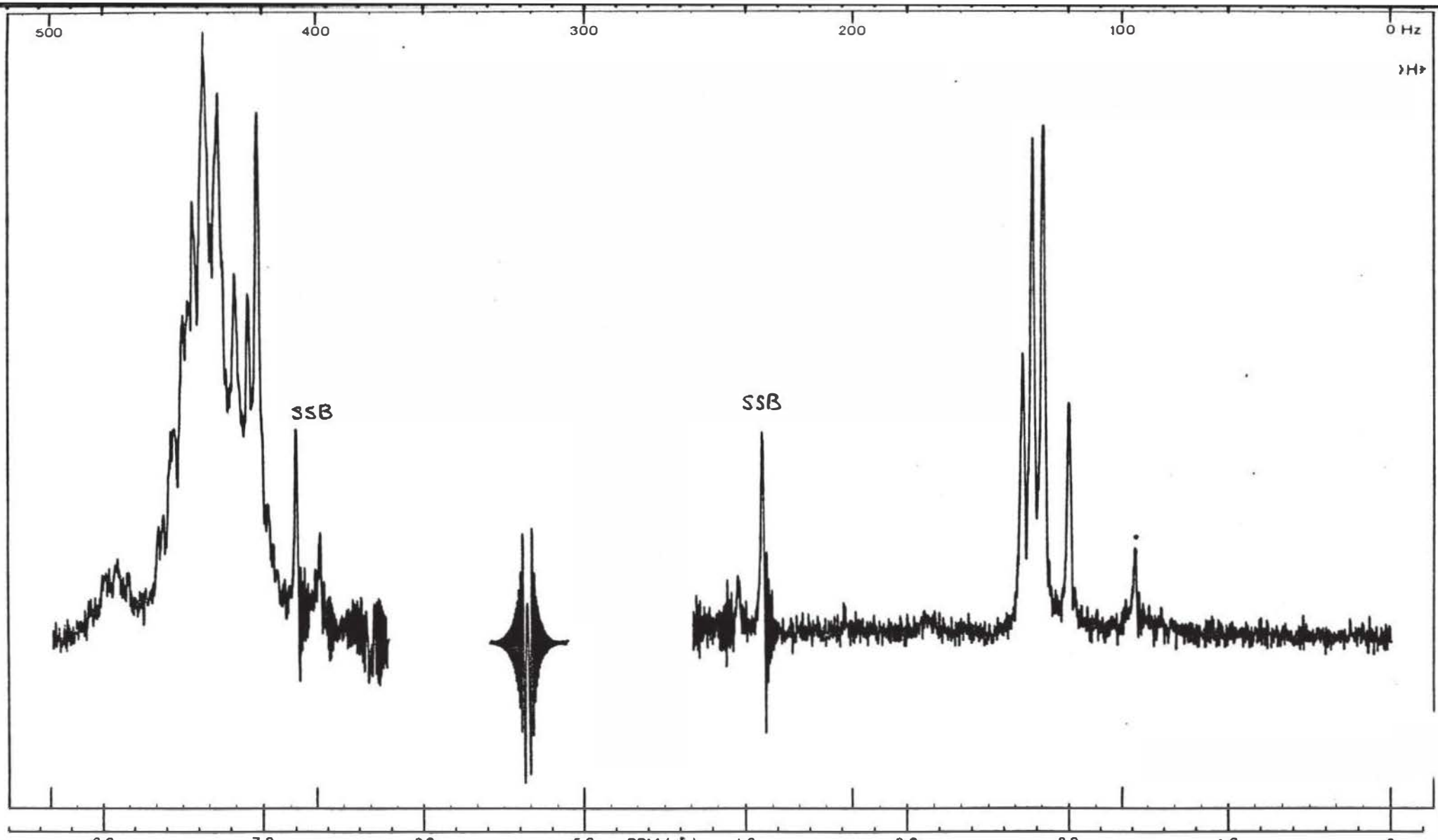
Figure 19

^{1}H nmr spectrum of $Ru(CO)(Cl)_2(Ph_2MeP)_3$ prepared by ligand exchange in CH_2Cl_2



SWEEP OFFSET (Hz): 000
SPECTRUM AMPLITUDE: 63
INTEGRAL AMPLITUDE: .....
SPINNING RATE (RPS): 40

MANUAL

SWEEP TIME (SEC): 50 ~~200~~ 500 1000 — AUTO ☐ (250)
SWEEP WIDTH (Hz): 25 50 100 250 ~~500~~ — (500)
FILTER: X 2 3 4 5 6 7 8 — (2)
RF POWER LEVEL: .03 — (05)

SAMPLE: $(\phi_2PMe)_3Ru(CO)Cl_2$
SOLVENT: CH_2Cl_2
DEC. LEVEL

REMARKS: CH_2Cl_2 Lock. Fig 2a (2)

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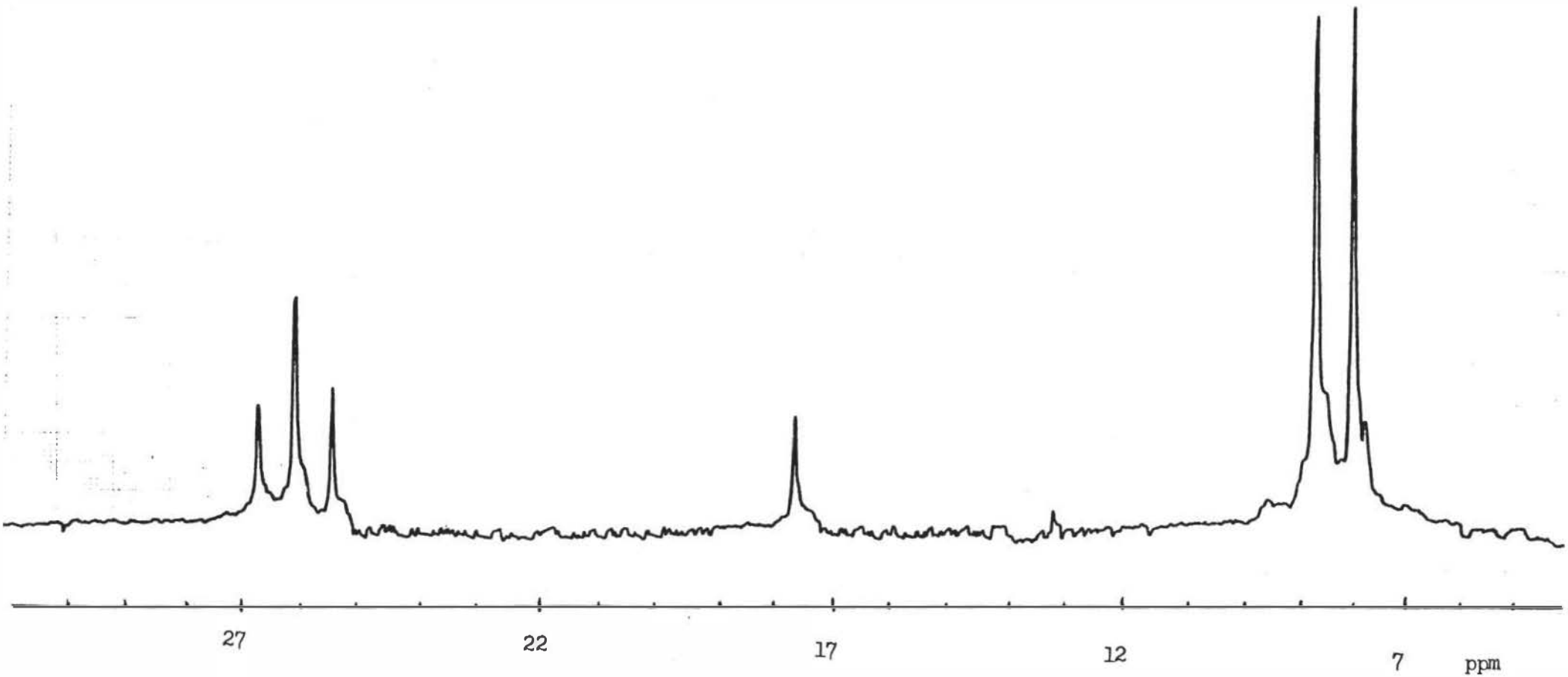
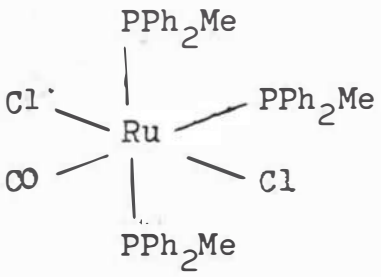
Figure 20

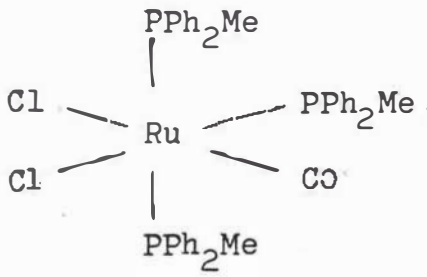
^{31}P nmr spectrum of $Ru(CO)(Cl)_2(Ph_2MeP)_3$


27
22
17
12
7
ppm

observed at 8.33 ppm (J_{PP} = 25.8 Hz), a singlet at 17.66 ppm and a triplet (relative area = 1) at 26.28 ppm (J_{PP} = 26.1 Hz). The doublet indicates that two of the phosphine ligands are located cis to the remaining phosphine ligand. The triplet corresponds to a diphenylmethyl ligand split by two equivalent phosphorous atoms. This spectrum substantiates the ^1H nmr spectrum. The singlet seen in the spectrum at 17.66 ppm is attributed to a triphenylphosphine containing impurity. The presence of this impurity was previously indicated by the depressed melting point of this compound and extraneous bands in the infrared spectrum. On the basis of the ^1H and ^{31}P spectra two possible isomeric structures can be suggested:



I-A



I-B

The isomers I-A and I-B could not be unequivocally distinguished from the available nmr data but structure I-B might be preferred since strong σ-donor ligands are generally trans to π-acceptor ligands as in cis-$Ru(CO)_2(Cl)_2(PPh_3)_2$ (14).

3. Synthesis of dichlorocarbonyltris(dimethylphenylphosphine)ruthenium (II), $Ru(CO)(Cl)_2((C_6H_5)(CH_3)_2P)_3$

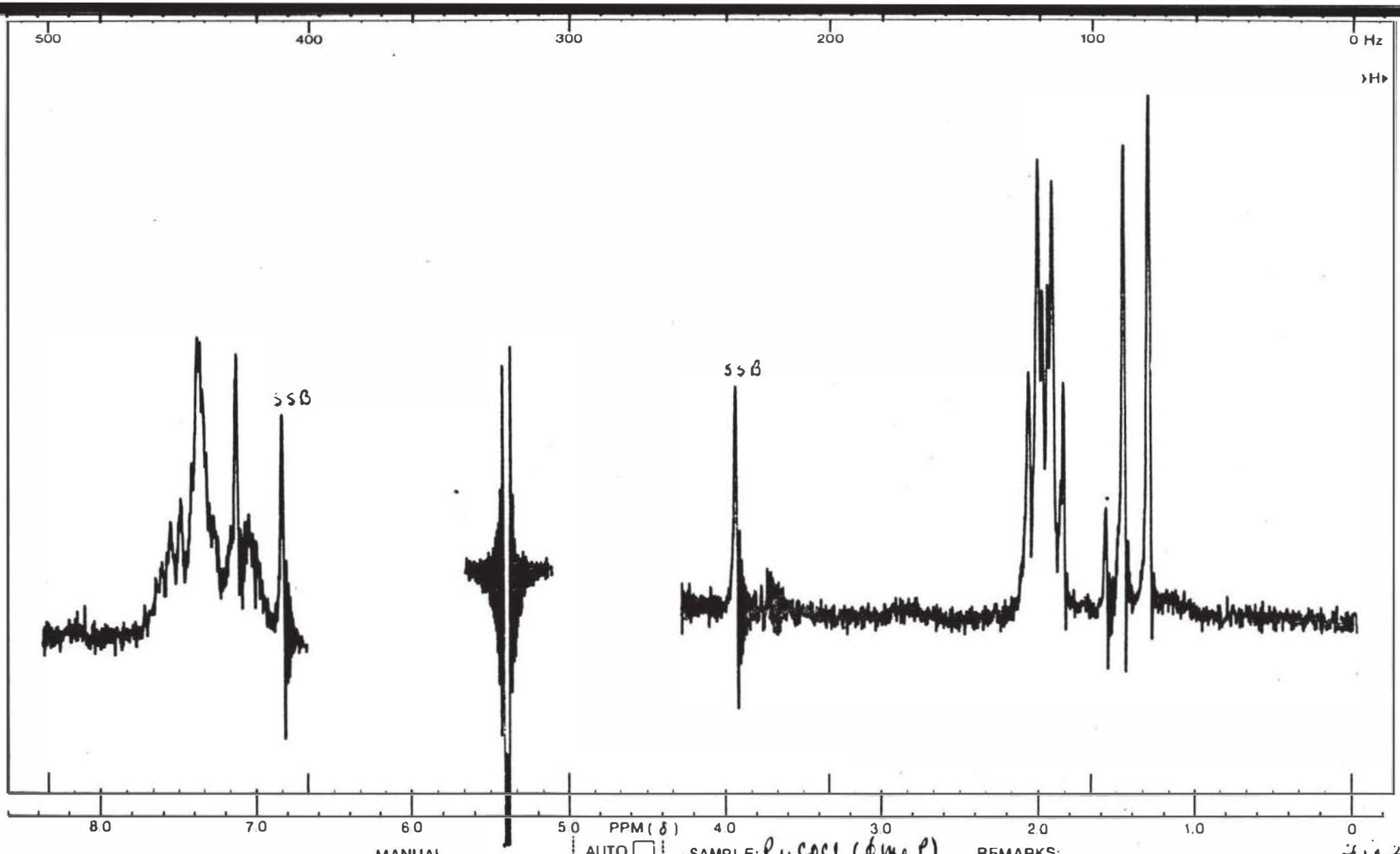
This complex was made successfully using the heterogeneous ligand exchange procedure adapted from the work of Armit and Stephenson (8). Only the starting material and an unidentified compound was obtained when the method based on the procedure of Chatt, Shaw and Field (7) was used. The compound, made by the ligand exchange method, showed a yield of 88%. Elemental analysis agrees with the suggested empirical formula. The melting point range for the complex was 173-175°C where the literature (9) gave a value of 179-181°C. The depressed melting point indicates that there is an impurity in the isolated material. The infrared data compared favorably with that reported in the literature (9): ν(C≡O), 1945 cm^{-1}; ν(C≡O), 1950 cm^{-1} (lit). Two small bands appearing at 2060 and 2000 cm^{-1} also indicates a small amount of impurity which may originate in the synthesis of the starting material, $Ru(CO)(Cl)_2(Ph_3P)_3$. C. Mooney (12) has since demonstrated that recrystallization of the product from methanol yielded a purer material. The infrared spectrum of the recrystallized white solid showed the absence of these bands at 2060 and 2000 cm^{-1}. These results also explain the compound's lower value for the melting point.

A ^1H nmr spectrum (Figure 21) was taken of the isolated complex. A doublet at 1.38 ppm (J_{PH} = 4.3 Hz) was seen indicating a methyl group that is coupled to only a single phosphorous nucleus in the material. Two overlapped triplets were observed at 1.93 ppm (J_{PH} = 3.4 Hz) and 2.02 ppm (J_{PH} = 3.3 Hz). Also a multiplet at 7.4 ppm which corresponds to the resonance arising from the phenyl groups of the ligand was detected. The two overlapping triplets suggests the existence of two species

Figure 21

^{1}H nmr spectrum of $Ru(CO)(Cl)_2(PhMe_2P)_3$

in CH_2Cl_2



MANUAL AUTO ☐

SWEEP OFFSET (Hz): .....
SPECTRUM AMPLITUDE: 6.3
INTEGRAL AMPLITUDE: .....
SPINNING RATE (RPS): 50

SWEEP TIME (SEC): 50 250 500 1000 (250)
SWEEP WIDTH (Hz): 25 50 100 250 500 (500)
FILTER: X 2 3 4 5 6 7 8 (2)
RF POWER LEVEL: .03 (.05)

SAMPLE: $RuCOCl_2(\phi Me_2P)_3$
SOLVENT: CH_2Cl_2
DEC. LEVEL

REMARKS: fig 2f
Lock on CH_2Cl_2

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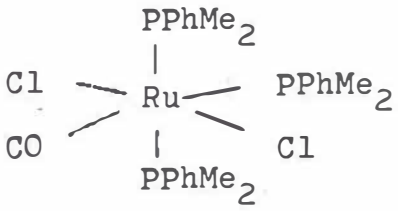
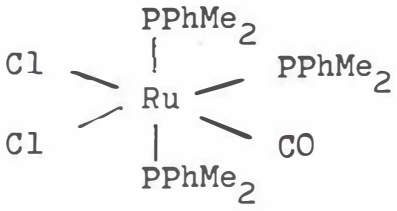
in solution with mutually trans phosphine ligands. Apparently the resonance of the cis phosphine ligand in each species occurs at the same chemical shift value (doublet at 1.38 ppm). The peak shown at 1.6 ppm is an impurity that comes from the solvent methylene chloride.

Figure 22 shows the ^{31}P nmr spectrum of this material. A triplet at 17.74 ppm (J_{PP} = 27.4 Hz) indicates that one phosphine ligand is split by two equivalent phosphorous atoms of the remaining ligands while the doublet at -1.42 ppm (J_{PP} = 27.1 Hz) indicates that two phosphorous ligand atoms in a trans configuration are split by one phosphorous atom in a cis ligand. No evidence for two species was detected in the ^{31}P nmr spectrum. Two structures for the complex, which are in accord with the observed nmr spectra are proposed below:



II-A



II-B

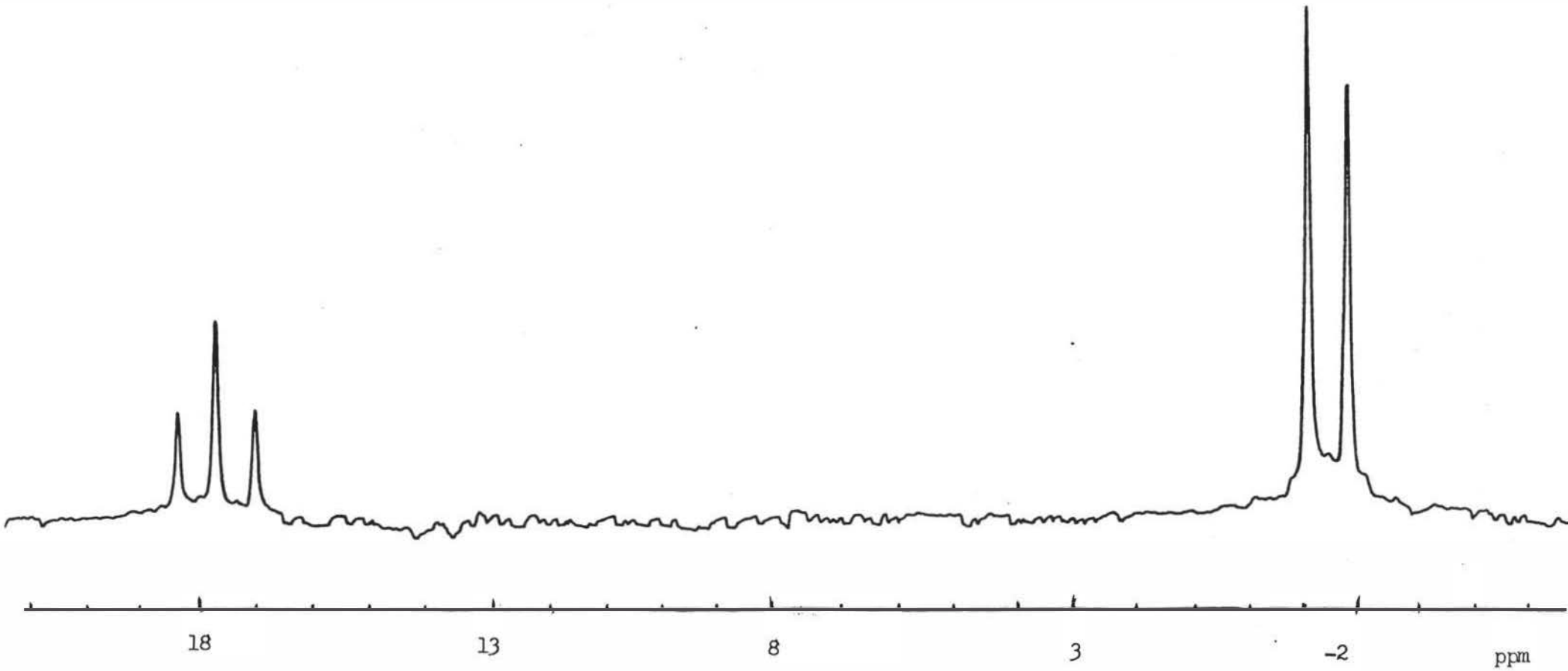
Possibly both of these isomers are present in methylene chloride solution as indicated by the ^{1}H nmr spectrum.

4. Synthesis of dichlorocarbonyltris(triethylphosphine)-ruthenium (II), $Ru(CO)(Cl)_2(Et_3P)_3$

The synthesis of this complex was tried using a variation

Figure 22

^{31}P nmr spectrum of $Ru(CO)(Cl)_2(PhMe_2P)_3$


18
13
8
3
-2
ppm

of a procedure described by Armit and Stephenson (8). A sample of $Ru(CO)(Cl)_2(Ph_3P)_3$ was refluxed in hexane under nitrogen with a six-fold excess of triethylphosphine. The solid in the suspension changed from bright yellow to pale yellow and diminished markedly in amount. Upon cooling an oil formed in the reaction mixture. The desired product could not be obtained even though the oil partially solidified to a gum. Using column chromatography, the product could not be separated from the starting material or separated from by-products to give a crystalline solid. At least two types of triethylphosphine compounds appear to be present from the ^1H nmr spectrum. Most likely the mixture contains some $Ru(CO)(Cl)_2(Et_3P)_3$ and some $Ru(CO)(Cl)_2(Et_3P)_2(Ph_3P)$. If only these two species are assumed, then the mixture appears to be 30 m% $Ru(CO)(Cl)_2(Et_3P)_3$ and 70 m% $Ru(CO)(Cl)_2(Et_3P)_2(Ph_3P)$.

B. Polarography and voltammetry of dichlorocarbonyltris(diphenylmethylphosphine)ruthenium (II) and dichlorocarbonyltris(dimethylphenylphosphine)ruthenium (II).

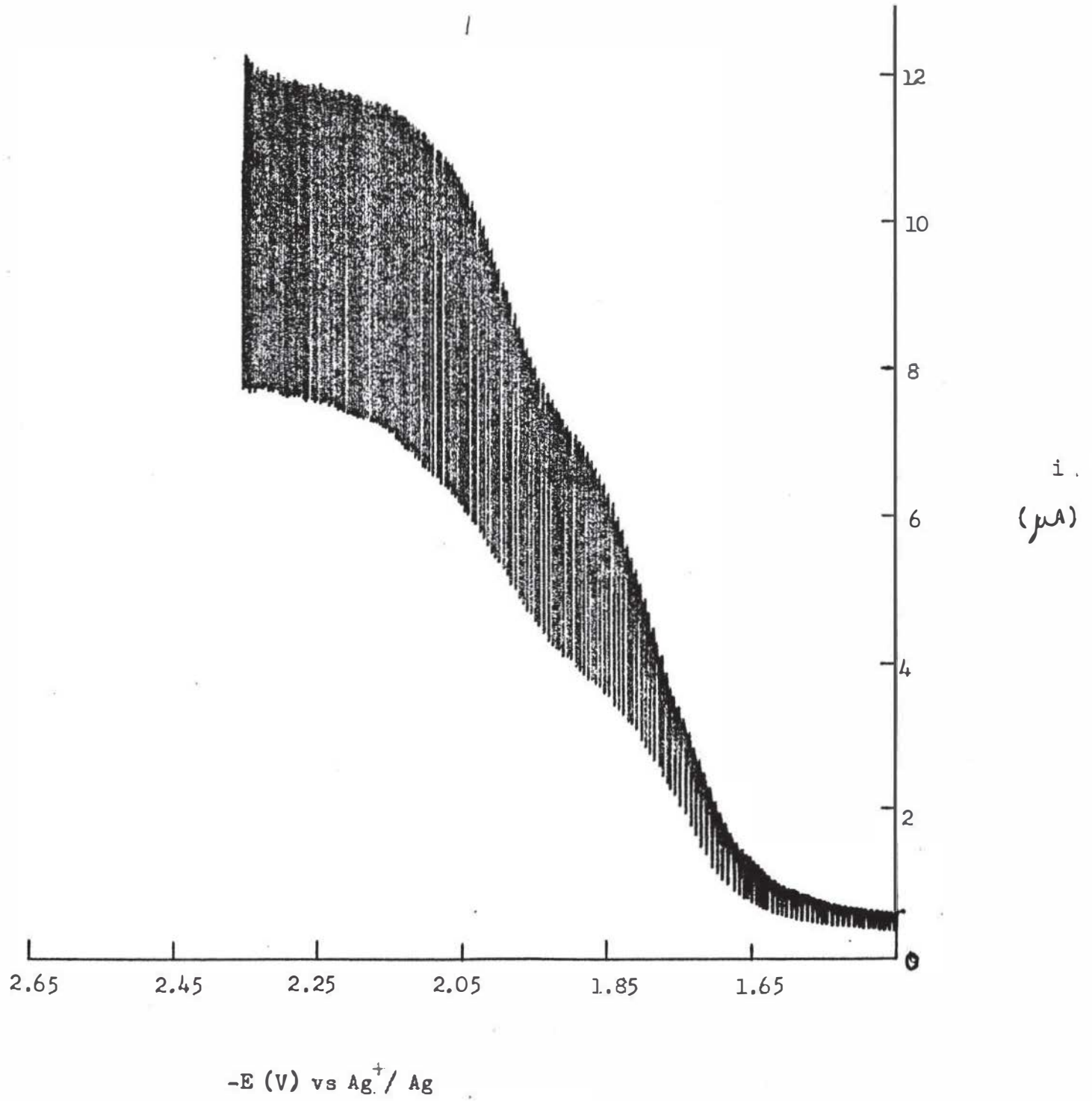
1. $Ru(CO)(Cl)_2((C_6H_5)_2(CH_3)P)_3$

The redox behavior of $Ru(CO)(Cl)_2((C_6H_5)_2(CH_3)P)_3$ was determined in acetonitrile at a dropping mercury and a spherical platinum electrode using polarography and cyclic voltammetry, respectively. A typical polarogram for this complex is shown in Figure 23. The reduction proceeds in two steps with the half-wave potential, $E_{\frac{1}{2}}$, for the first wave at -1.78 V and

Figure 23

Polarogram of 1.00×10^{-3}M $Ru(CO)(Cl)_2(Ph_2MeP)_3$

in acetonitrile


12
10
8
6
4
2
0
i
(μA)
2.65
2.45
2.25
2.05
1.85
1.65
-E (V) vs Ag+/ Ag

for the second wave at -2.00 V. Comparison of the total limiting current for these reductions with that of $RuCl_2((C_6H_5)_3P)_4$, which is known to undergo an overall two electron reduction process (1), indicates that two electrons are also transferred in this reduction sequence. The ratio of the limiting current of the first wave to that of the second wave is 1.44 (Table 3), which indicates that the reduction steps arise not from the sequential addition of a single electron to one solution species but from two electron reductions of two distinct solution species. Similar behavior has been previously observed for non-carbonyl containing tertiary phosphine complexes of ruthenium (II) (1).

The limiting current for each reduction was dependent on the mercury column height as shown in Table 4. The dependence of limiting current on mercury column height was determined by plotting log i_l vs log h for each reduction wave (Figure 24). The slope of the line for the first reduction wave is 0.60 $\pm$ .07 and for the second 0.48 $\pm$ .08. Mass transport of the electroactive species to the electrode surface by only diffusion should yield a slope of 0.50. The measured slopes indicate that both reduction processes are under diffusion control predominantly. For the first wave the limiting current appears to be independent of mercury column height at the highest value of the height (shortest drop time). Such behavior suggests that kinetic control of mass transport may become important at short drop times. For a totally kinetic controlled reduction process the limiting current is independent of mercury column height.

Table 3

Polarographic Parameters for

$Ru(CO)(Cl)_2(Ph_2MeP)_3$ and $Ru(CO)(Cl)_2(PhMe_2P)_3$ in Acetonitrile

Complex	Concentration	Excess Ligand Complex	h, cm	1st Wave		2nd Wave	
				$E_{\frac{1}{2}}$, V	i_l, μA	$E_{\frac{1}{2}}$, V	i_l, μA
$Ru(CO)(Cl)_2(Ph_2MeP)_3$	$1.00 \pm .01 \times 10^{-3}$	-	75.0±.1	-1.78±.05	6.24±.05	-2.09±.05	4.34±.05
$Ru(CO)(Cl)_2(Ph_2MeP)_3$	$1.00 \pm .01 \times 10^{-3}$	1	75.0	-1.68	4.24	-1.91	3.00
$Ru(CO)(Cl)_2(PhMe_2P)_3$	$1.00 \pm .01 \times 10^{-3}$	-	75.0	-1.95	3.00	-2.26	6.98

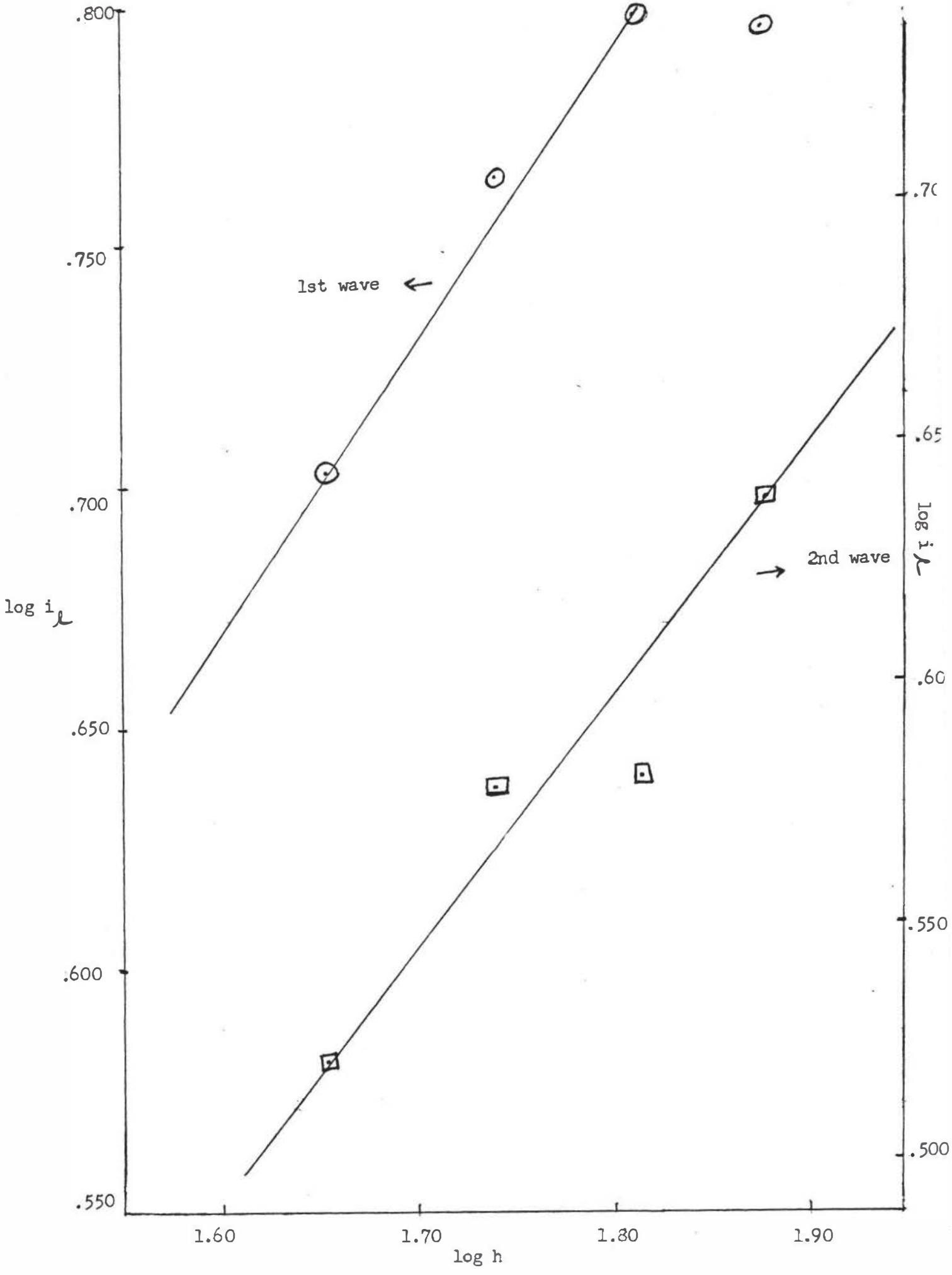
Table 4

Effect of Column Height on the Limiting Current of 1.00×10^{-3}M $Ru(CO)(Cl)_2(Ph_2MeP)_3$

h, cm	$(i_l)_{total}$, μA	$(i_l)_1$, μA	$(i_l)_2$, μA
75.0 ± .1	10.58 ± .05	6.24 ± .05	4.34 ± .05
65.0	10.08	6.28	3.80
55.0	9.59	5.81	3.78
45.0	8.37	5.05	3.32

Figure 24

Limiting current for first and second reduction waves for 1.00×10^{-3} M $Ru(CO)(Cl)_2(Ph_2MeP)_3$ as function of mercury height.


.800
.750
.700
.650
.600
.550
log i_ℓ
1st wave
2nd wave
.70
.65
.60
.550
.500
log i_ℓ
1.60
1.70
1.80
1.90
log h

When excess Ph_2MeP was added, the polarographic waves (Figure 25) became more drawn out. The $E_{\frac{1}{2}}$ of each wave was shifted to -1.68 V and -1.91 V, respectively. The limiting current for the first and second reduction waves decreased to 4.24 μA and 3.00 μA, respectively. In the presence of excess Ph_2MeP the limiting currents of each reduction process also depended on the mercury column height (Table 5). Analysis of the height dependence for each wave (Figure 26) yields slopes of 0.06 $\pm$ .01 and 0.33 $\pm$ .07 for the first and second waves, respectively. The first wave appears to be almost under complete kinetic control since the limiting current is approximately independent of mercury column height. Kinetic control for this reduction step was only detected at the shortest drop times employed in the absence of excess ligand (Figure 24). The second reduction step shows a mixture of diffusion and kinetic control which leads to a slope value between zero and 0.50. The change from diffusion to kinetic control in the presence of excess ligand explains the observed decrease in the limiting currents for each wave. This change in mass transport mode could also contribute to the observed shift in $E_{\frac{1}{2}}$ for each process.

A cyclic voltammogram of $Ru(CO)(Cl)_2(Ph_2MeP)_3$ in CH_3CN, using a spherical platinum electrode, exhibited two peaks at -1.84 V and -2.13 V during the cathodic sweep (Figure 27). The voltammogram showed that the reaction was totally irreversible since no anodic peaks were observed in the potential regions where the reductions occured. A voltammogram was also taken of the solution with excess Ph_2MeP as shown in Figure 28.

Figure 25

Polarogram of 1.00×10^{-3}M $Ru(CO)(Cl)_2(Ph_2MeP)_3$ in the presence of excess Ph_2MeP in acetonitrile

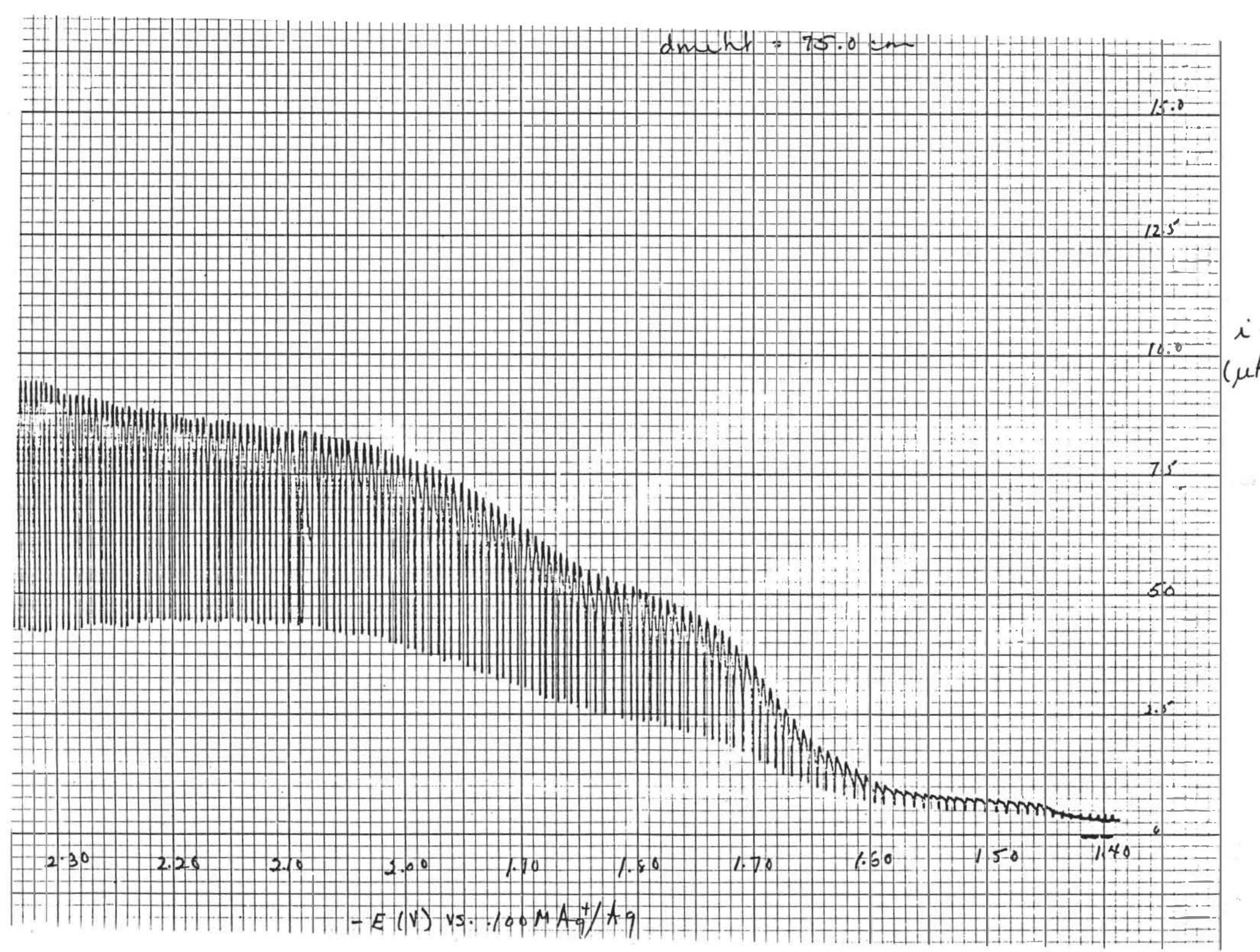

dmuht = 75.0 cm
15.0
12.5
10.0
7.5
5.0
2.5
i
(μ
2.30
2.20
2.10
2.00
1.90
1.80
1.70
1.60
1.50
1.40
-E (V) vs. .100 M Ag+/Ag

Table 5

Dependence of Limiting Current on Mercury Column Height for 1.00×10^{-3}M $Ru(CO)(Cl)_2(Ph_2MeP)_3$ with 1.00×10^{-3}M excess Ph_2MeP

h, cm	$(i_\ell)_1$, μA	$(i_\ell)_2$, μA
75.0 ± .1	4.24 ± .05	3.00 ± .05
65.0	4.25	2.80
55.0	4.18	2.78
45.0	4.11	2.50

Figure 26

Log i_l vs log h for reduction waves of $Ru(CO)(Cl)_2(Ph_2MeP)_3$ with single-fold excess of Ph_2MeP.

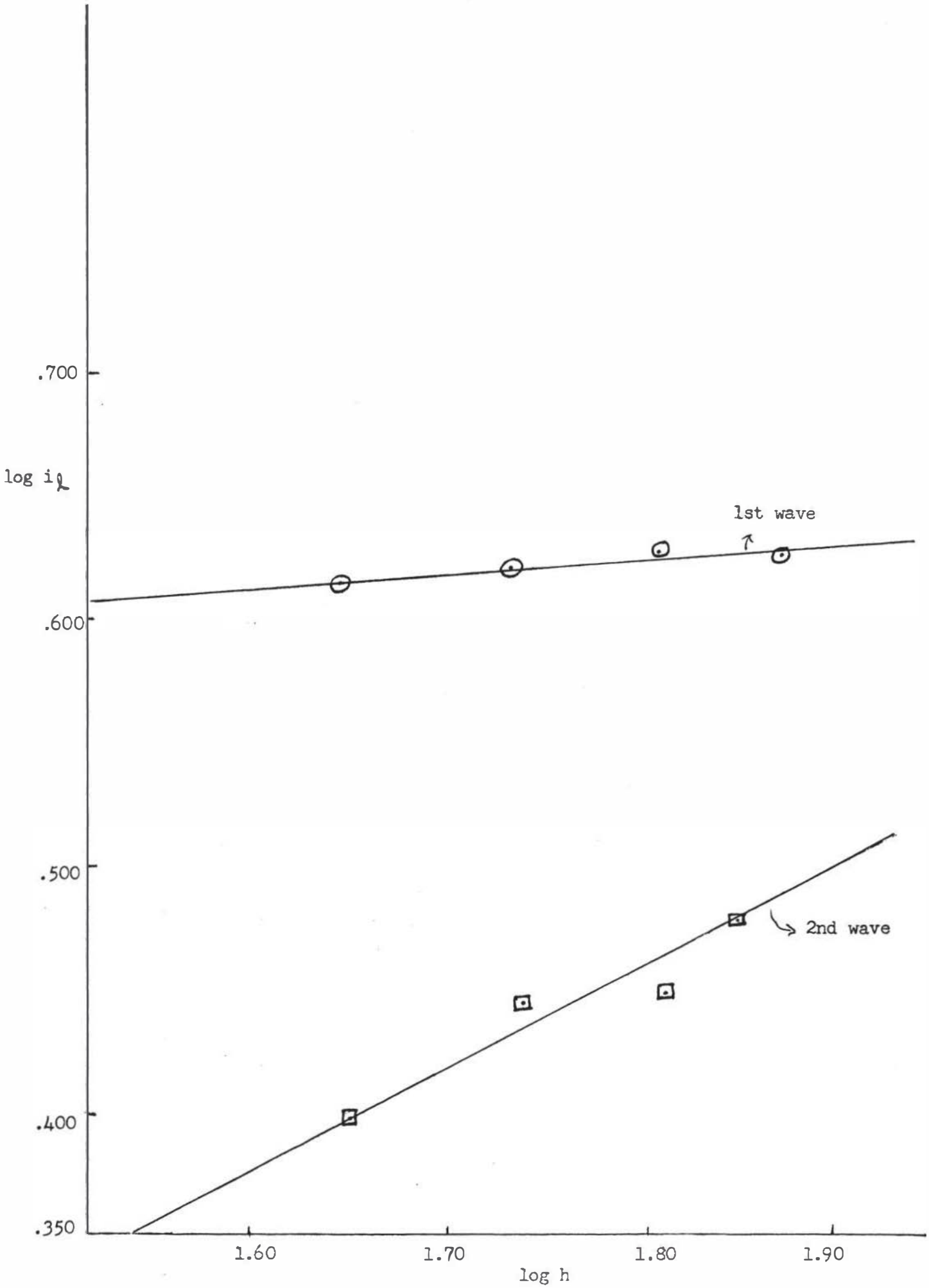

.700
log i_l
1st wave
.600
.500
2nd wave
.400
.350
1.60
1.70
1.80
1.90
log h

Figure 27

Voltammogram of 1.00×10^{-3}M $Ru(CO)(Cl)_2(Ph_2MeP)_3$ in acetonitrile

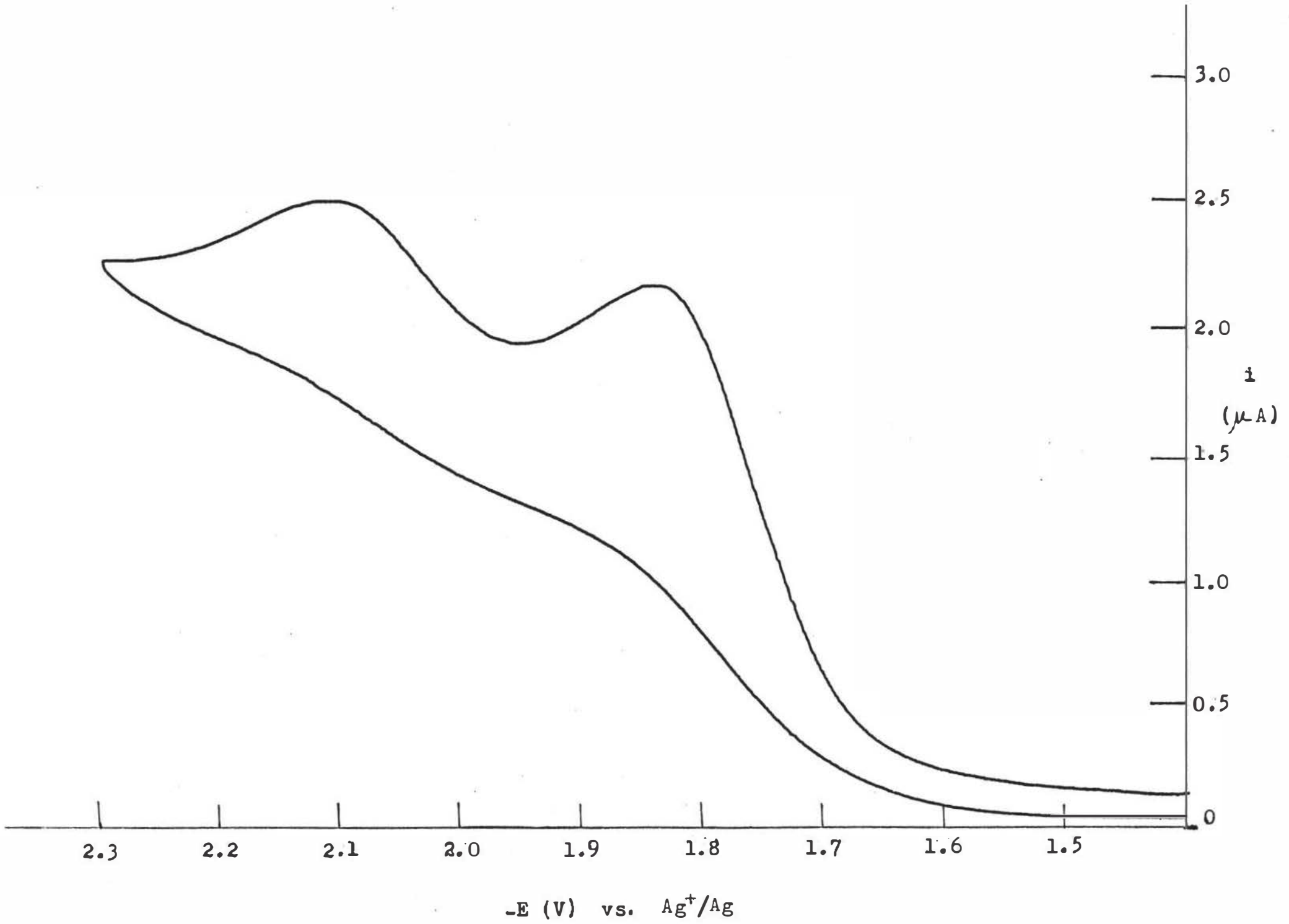
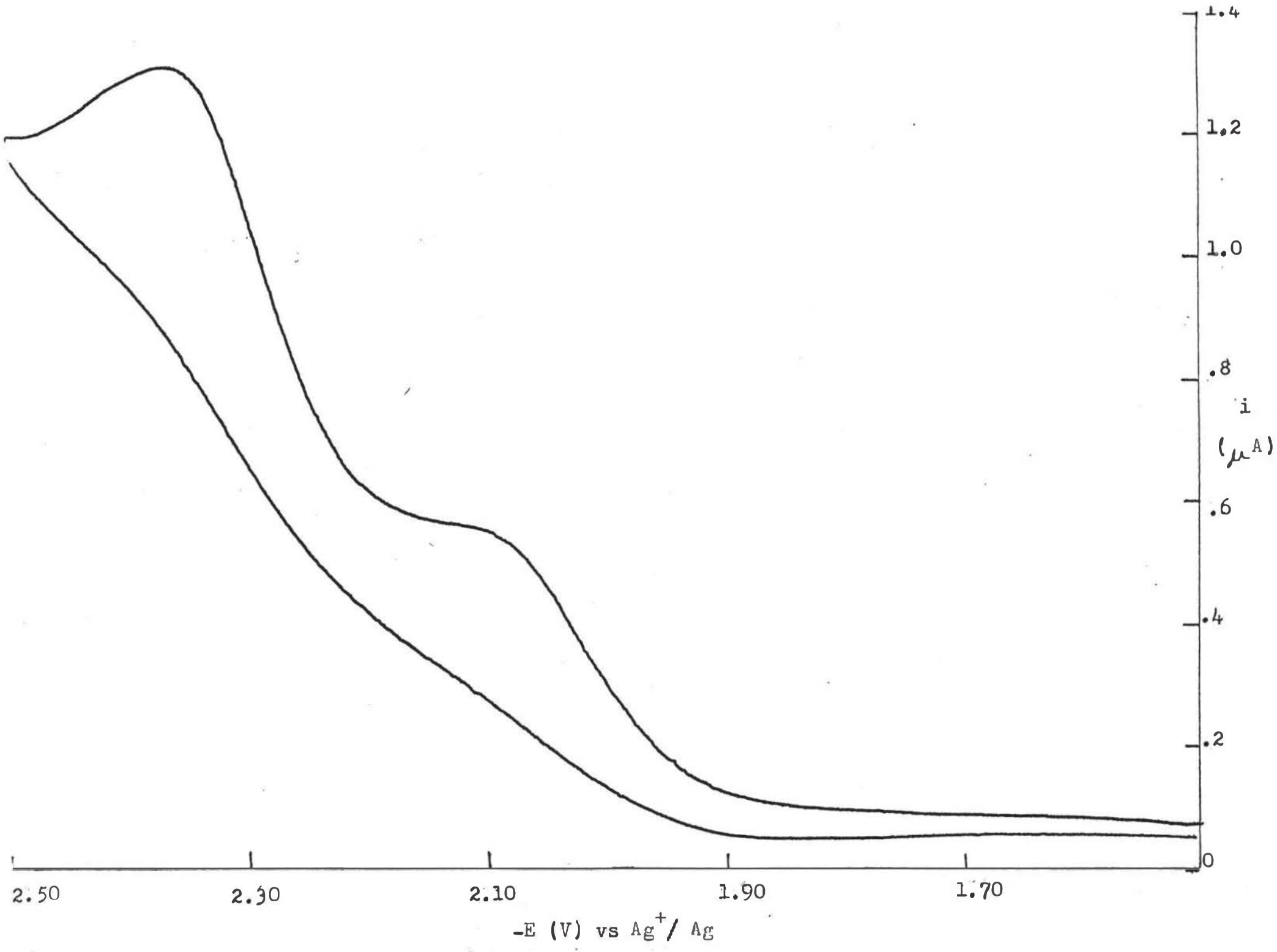

3.0
2.5
2.0
i
(μA)
1.5
1.0
0.5
0
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
-E (V) vs. Ag+/Ag

Figure 28

Voltammogram of 1.00×10^{-3}M $Ru(CO)(Cl)_2(Ph_2MeP)_3$ in the presence of 1.00×10^{-3}M Ph_2MeP in acetonitrile


1.4
1.2
1.0
.8
i
(μA)
.6
.4
.2
0
2.50
2.30
2.10
1.90
1.70
-E (V) vs Ag+/ Ag

The potential of each peak was shifted cathodically to -1.93 V and -2.25 V, respectively. The two peaks observed in the voltammogram supports a sequential two-electron reduction of two different complexes formed in solution.

Since $Ru(CO)(Cl)_2(Ph_2MeP)_3$ is coordinatively saturated, the two species formed in acetonitrile, which give rise to the two reduction steps observed, most likely arise from ligand exchange with the solvent. Either Ph_2MeP or the chloride ligands could possibly undergo such a metathesis reaction. In the case of exchange of Ph_2MeP the following reduction scheme seems plausible.

$$Ru(CO)(Cl)_2(Ph_2MeP)_3 + CH_3CN \rightleftharpoons Ru(CO)(Cl)_2(Ph_2MeP)_2(CH_3CN) + Ph_2MeP$$

$$Ru(CO)(Cl)_2(Ph_2MeP)_2(CH_3CN) + 2e + Ph_2MeP \rightarrow Ru(CO)(Ph_2MeP)_3(CH_3CN) + 2Cl^-$$

$$Ru(CO)(Cl)_2(Ph_2MeP)_3 + 2e + CH_3CN \rightarrow$$

The suggested formula for the postulated reduction product is identical to that observed for the product of electrochemical reduction of the analogous $Ru(CO)(Cl)_2(Ph_3P)_3$ in acetonitrile (vide infra). Loss of a phosphine ligand in this solvent has been observed for $Ru(CO)(Cl)_2(Ph_3P)_3$ with dimer formation as discussed previously. Since replacement of solvent by a ligand is usually accompanied by a cathodic shift in half-wave potential, $Ru(CO)(Cl)_2(Ph_2MeP)_2(CH_3CN)$ would be expected to be reduced at a less negative potential than $Ru(CO)(Cl)_2(Ph_2MeP)_3$. Thus according to this scheme the initial wave results from the

reduction of the acetonitrile containing complex while the second wave is attributed to the reduction of $Ru(CO)(Cl)_2(Ph_2MeP)_3$. The observed height of the first wave to that of the second wave was 1.44:1 which indicates that the acetonitrile containing complex is favored and, hence, the exchange equilibrium lies to the right. This interpretation must be regarded as tentative since the relation of half-wave potential to degree of coordination is only strictly applicable for reversible systems and the reduction steps for $Ru(CO)(Cl)_2(Ph_2MeP)_3$ are irreversible.

The relatively high dielectric constant of acetonitrile also suggests that exchange of chloride ions leading to ionic species is a reasonable alternative to exchange of Ph_2MeP. The proposed reduction scheme for this case can be represented as follows:

$$Ru(CO)(Cl)_2(Ph_2MeP)_3 + CH_3CN \rightleftharpoons (Ru(CO)(Cl)(Ph_2MeP)_3(CH_3CN))^+ + Cl^-$$

$$(Ru(CO)(Cl)(Ph_2MeP)_3(CH_3CN))^+ + 2e \searrow$$

$$Ru(CO)(Ph_2MeP)_3(CH_3CN) + Cl^-$$

$$Ru(CO)(Cl)_2(Ph_2MeP)_3 + CH_3CN + 2e \nearrow$$

Similar reduction schemes have been proposed for the reduction of non-carbonyl ruthenium (II) complexes of the type $RuCl_2(R_3P)_4$ in acetonitrile (1). By an argument similar to that proposed above for phosphine exchange the first wave could be assigned to the reduction of $(Ru(CO)(Cl)(Ph_2MeP)_3(CH_3CN))^+$ and the second wave to the reduction of $Ru(CO)(Cl)_2(Ph_2MeP)_3$.

The observed change in shape, i_ℓ and $E_{\frac{1}{2}}$ of the reduction waves upon addition of excess Ph_2MeP suggests that exchange of the phosphine ligand seems more probable than chloride exchange. Further variation in the amount of excess phosphine is needed to verify this conclusion. Also a study of the conductivity of acetonitrile solutions of $Ru(CO)(Cl)_2(Ph_2MeP)_3$ would serve to determine the importance, if any, of chloride metathesis. The observed magnitude of the total limiting current for both reduction steps both in the presence and absence of excess ligand indicates that dimer formation need not be considered.

Inspection of the polarographic and voltammetric data indicates that a potential of -2.38 V would be necessary to reduce both solution species. Since this potential is very close to that required for reduction of tetraethylammonium ion on platinum,

$$(C_2H_5)_4N^+ + e \rightleftharpoons (C_2H_5)_3N + C_2H_4 + \tfrac{1}{2}H_2$$

a mercury cathode should be employed for electrosynthesis.

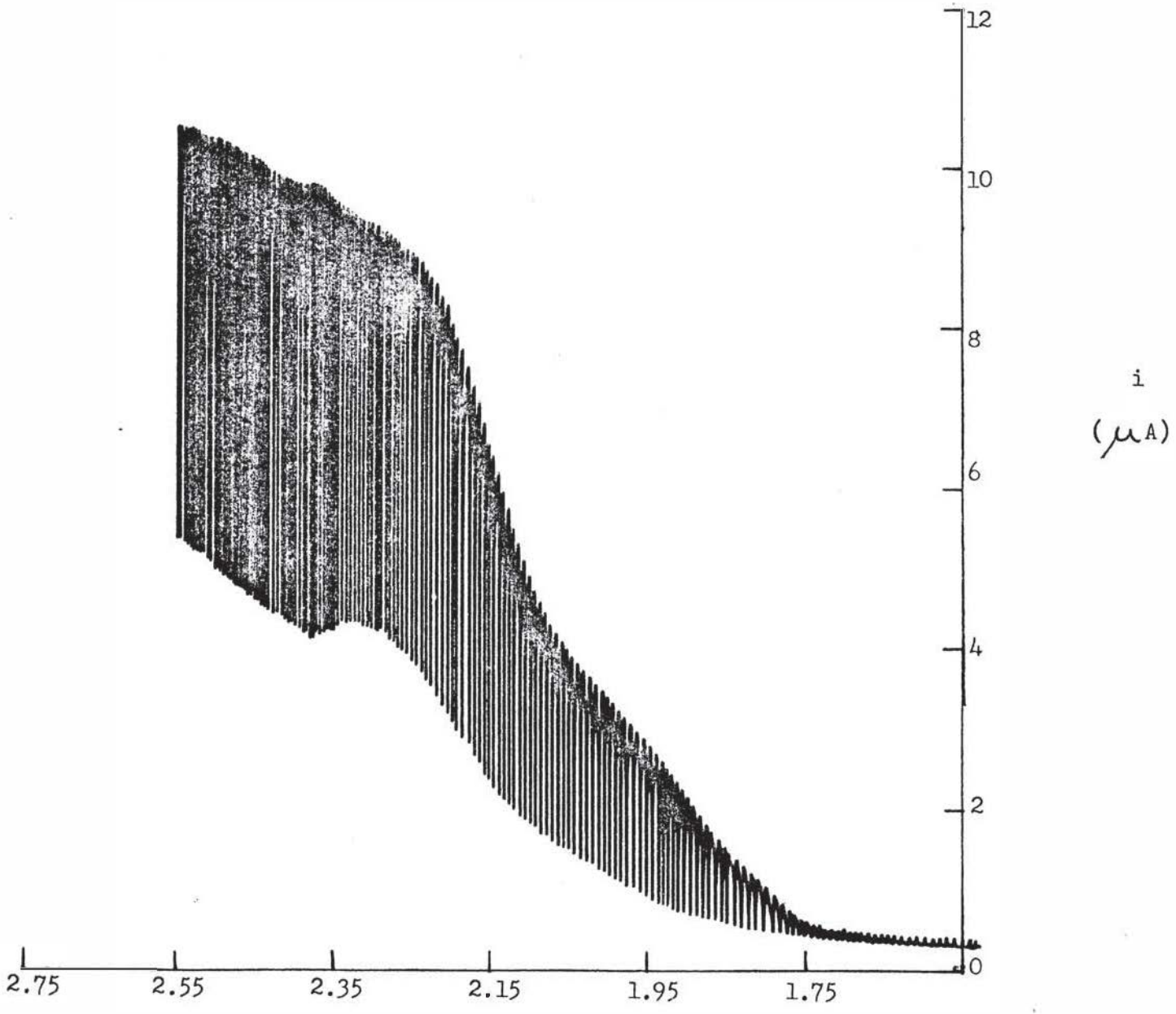
2. $Ru(CO)(Cl)_2((C_6H_5)(CH_3)_2P)_3$

The oxidation-reduction behavior of $Ru(CO)(Cl)_2((C_6H_5)(CH_3)_2P)_3$ was determined in CH_3CN at a dropping mercury and a spherical platinum electrode using polarography and cyclic voltammetry, respectively. The polarogram of the compound is illustrated in Figure 29. The reduction proceeded in two ill-defined steps with the half-wave potential for the first wave at -1.95 V

Figure 29

Polarogram of 1.00×10^{-3}M $Ru(CO)(Cl)_2(PhMe_2P)_3$

in acetonitrile


12
10
8
6
4
2
0
i
(μA)
2.75
2.55
2.35
2.15
1.95
1.75
-E vs Ag+ /Ag

and for the second wave at -2.26 V. Comparison of the total limiting current for these reductions with that of $Ru(Cl)_2((C_6H_5)_3P)_4$, which is known to undergo a two electron process (1), indicates that two electrons are also transferred in this reduction sequence. The ratio of the limiting current of the first wave to that of the second wave is 0.430 (Table 3), which indicates that the reduction steps arise not from the sequential addition of a single electron to one solution species but from the two electron reductions of two distinct solution species.

Although the polarographic behavior of $Ru(CO)(Cl)_2(PhMe_2P)_3$ is comparable to that of $Ru(CO)(Cl)_2(Ph_2MeP)_3$ in that the reduction involves the overall transfer of two electrons to two solution species, it was observed that the half-wave potentials of the reduction processes for $Ru(CO)(Cl)_2(PhMe_2P)_3$ occurred at more negative potentials and that the limiting current of the initial wave was in this case smaller than that for the second wave. The cathodic shift of the half-wave potential can be attributed to the increased donor strength of $PhMe_2P$ relative to that of Ph_2MeP. Such cathodic shifts with increasing donor strength are well known (15). The difference in relative magnitudes of the limiting currents of the two reduction steps further suggests that the two solution species result from ligand exchange with the solvent, but in the case of the dimethylphenylphosphine complex, this exchange is less extensive.

The limiting current for each reduction wave was dependent on the mercury column height as shown in Table 6. The data in

Table 6

Effect of Column Height on the Limiting Current of 1.00×10^{-3} M $Ru(CO)(Cl)_2(PhMe_2P)_3$

h, cm	$(i_l)_{total}$, μA	$(i_l)_1$, μA	$(i_l)_2$, μA
75.0 ± .1	9.98 ± .05	3.00 ± .05	6.98 ± .05
65.0	9.30	3.00	6.30
55.0	9.42	3.63	5.79
45.0	8.08	3.30	4.78

Table 6 were plotted as log i_ℓ vs log h for each reduction wave (Figure 30). The height dependence of the second wave (slope = 0.74) seems to be a mixture of diffusion and adsorption control. Absorption of an electroactive species at the electrode produces a current directly proportional to h (slope of log i_ℓ vs log h = 1). The height dependence of the first wave shows that the mass transport of electroactive species changes with h. At high heights (short drop time) i_ℓ is independent of h which indicates kinetic control while at lower heights, (larger drop time), the height dependence becomes diffusion controlled (slope for 2 lowest heights $=\sim .5$). This suggests that at short drop times the rate of current flow is limited by chemical reaction

$$X \xrightarrow{k} O + ne \rightleftharpoons R$$

where the rate constant determines how much O, which is reducible, is at the surface to be reduced. At longer lifetimes of the drop sufficient O is available around the drop and its diffusion becomes rate controlling. Similar behavior was also noted for the first reduction wave of $Ru(CO)(Cl)_2(Ph_2MeP)_3$.

The cyclic voltammogram (Figure 31) shows two peaks at -2.12 V and -2.39 V, respectively. The reductions are completely irreversible as shown by the absence of anodic peaks in the potential regions where the reductions are observed.

A similar reduction scheme to that proposed for the reduction of $Ru(CO)(Cl)_2(PhMe_2P)_3$ is in accord with the polarographic and voltammetric data. The suggested scheme is shown below

Figure 30

Limiting current for first and second reduction waves for 1.00×10^{-3} M $Ru(CO)(Cl)_2(PhMe_2P)_3$ as a function of mercury height

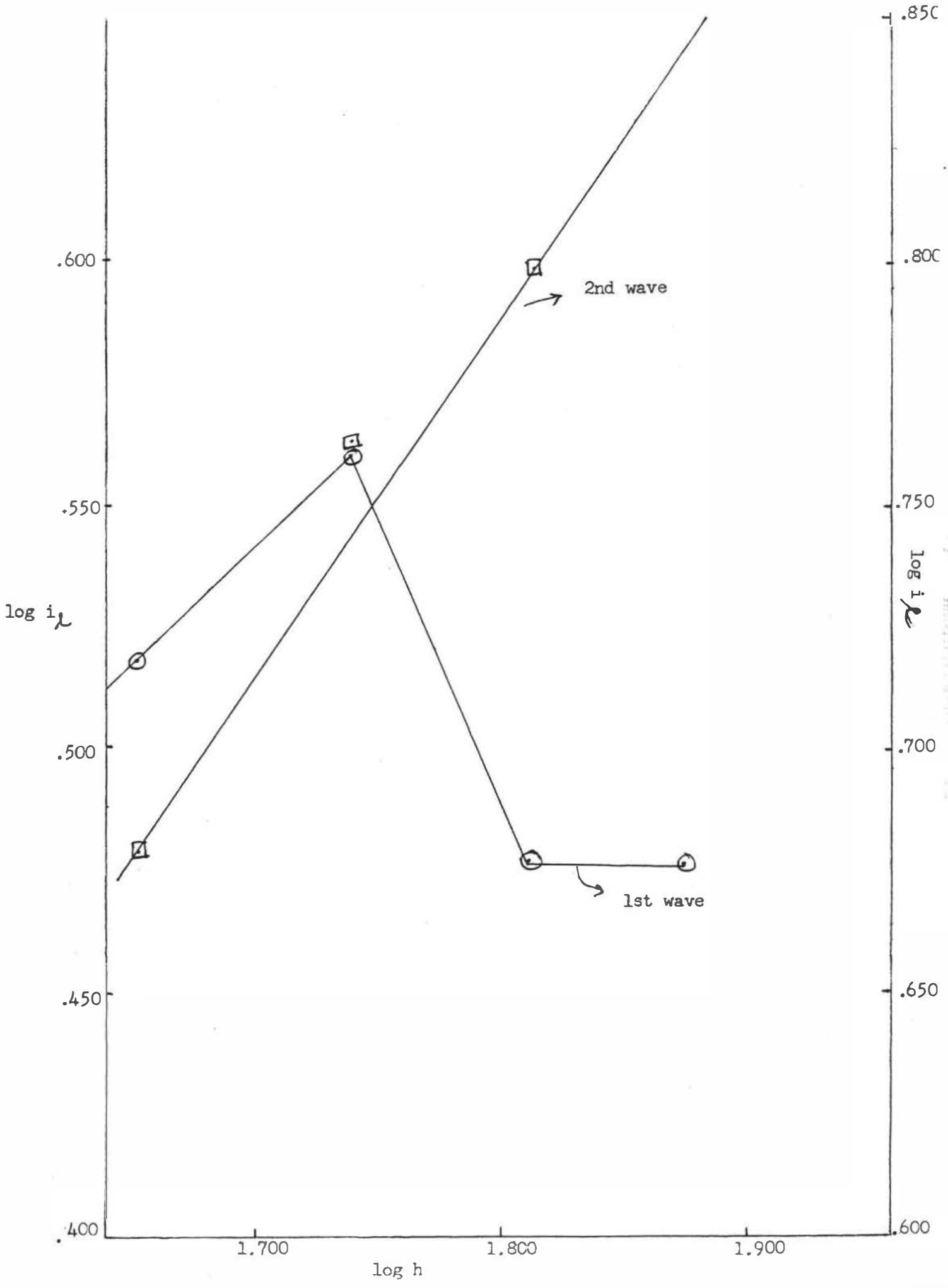
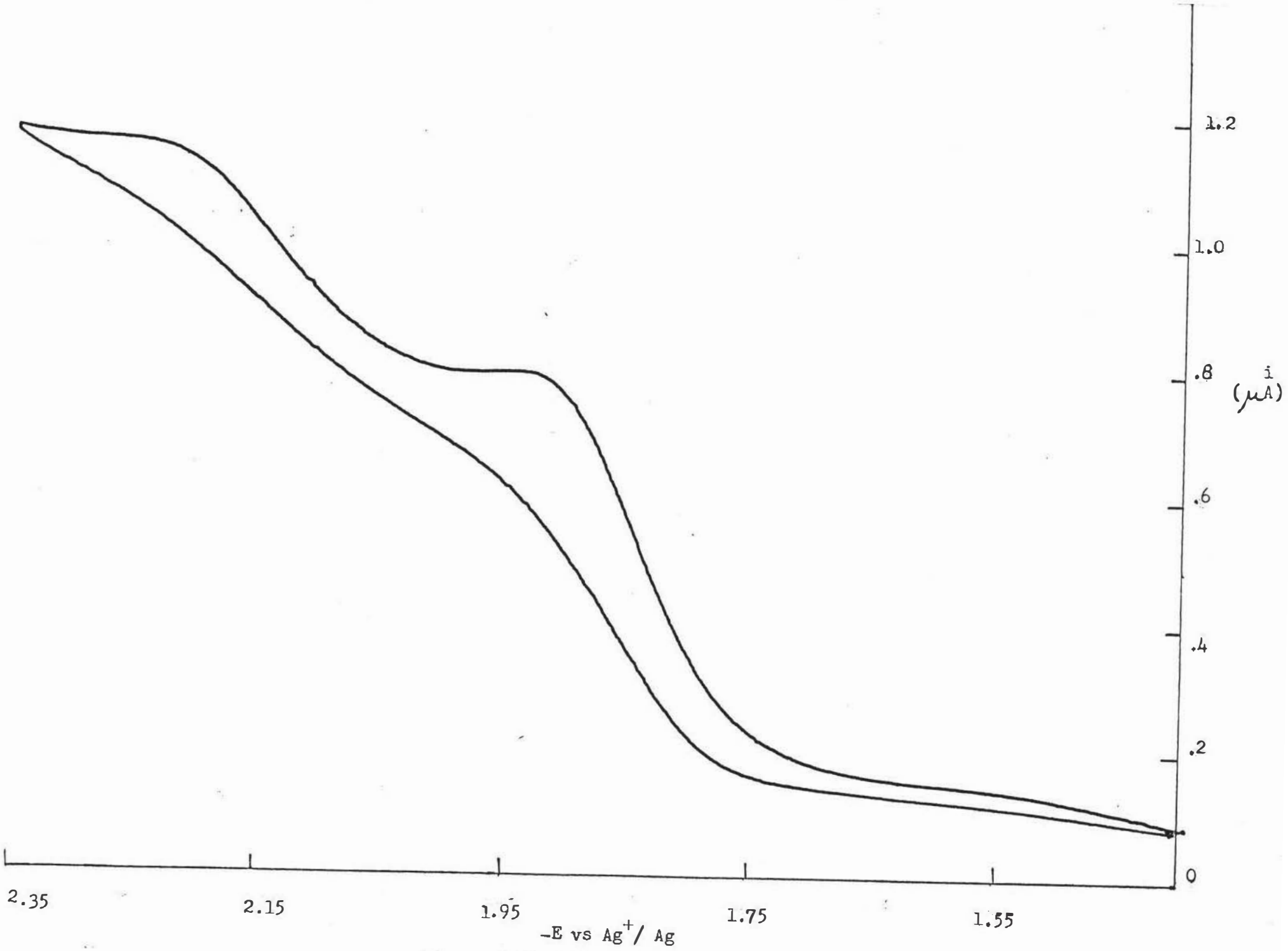

.850
.800
.750
.700
.650
.600
.600
.550
.500
.450
.400
log i_λ
log i_λ
2nd wave
1st wave
1.700
1.800
1.900
log h

Figure 31

Voltammogram of 1.00×10^{-3}M $Ru(CO)(Cl)_2(PhMe_2P)_3$

in acetonitrile


1.2
1.0
.8
i
(μA)
.6
.4
.2
0
2.35
2.15
1.95
1.75
1.55
-E vs Ag+/ Ag

$$Ru(CO)(Cl)_2(PhMe_2P)_3 + CH_3CN \rightleftharpoons Ru(CO)(Cl)_2(PhMe_2P)_2(CH_3CN) + PhMe_2P$$

$$Ru(CO)(Cl)_2(PhMe_2P)_2(CH_3CN) + 2e + PhMe_2P \searrow$$

$$Ru(CO)(Cl)_2(PhMe_2P)_3 + 2e + CH_3CN \longrightarrow Ru(CO)(PhMe_2P)_3(CH_3CN) + 2Cl^-$$

The product predicted from electron transfer has the same empirical formula as that observed from the reduction of $Ru(CO)(Cl)_2(Ph_3P)_3$ in acetonitrile. In this case the solvent/ligand exchange reaction proceeds to a much lesser extent than for the Ph_2MeP complex and $Ru(CO)(Cl)_2(PhMe_2P)_3$ appears to be the predominant solution species. The observed kinetic control of the first reduction wave (reduction of $Ru(CO)(Cl)_2(PhMe_2P)_2(CH_3CN)$) also suggests that this equilibrium is not as facile as in the case of the analogous Ph_2MeP compound. The addition of an additional ligand to generate the postulated product either simultaneous with or following electron transfer would account for the observed irreversibility of the reduction steps. The marked change in the reduction pattern observed for these two compounds with a change in phosphine ligand further suggests that phosphine exchange is important in generating the two solution species.

For electrosynthesis a potential of approximately -2.53 V would need to be employed and to achieve such potentials a mercury cathode would have to be used.

C. Synthesis of Ruthenium (0) complexes

1. Electrolysis of $Ru(CO)(Cl)_2(Ph_3P)_3$

The complex, $Ru(CO)(Cl)_2(Ph_3P)_3$, was electrolyzed at -2.30 V in the presence of excess triphenylphosphine in acetonitrile to produce $Ru(CO)(CH_3CN)(Ph_3P)_3$. The starting material was completely soluble in the catholyte whereas the starting material, $(Ru(CO)(Cl)_2(Ph_3P)_2)_2$, used by Olson (1) formed a suspension. The increased solubility of the starting material resulted in a 3 hour shorter electrolysis time. The red, air-sensitive complex, $Ru(CO)(CH_3CN)(Ph_3P)_3$, which separated from the catholyte, was identical to that reported by Olson (1) on the basis of its melting point and infrared spectrum. The reaction carried out was

$$Ru(CO)(Cl)_2(Ph_3P)_3 + CH_3CN + 2e \xrightarrow[Ph_3P]{xs.} Ru(CO)(CH_3CN)(Ph_3P)_3 + 2Cl^-$$

Excess triphenylphosphine in the catholyte was necessary to prevent formation of the dimer, $(Ru(CO)(Cl)_2(Ph_3P)_2)_2$, in the acetonitrile solvent. No precipitate formation was observed when $Ru(CO)(Cl)_2(Ph_3P)_3$ was added to the solvent containing excess Ph_3P. The compound was obtained in an 80% yield (lit. value: 88% yield). Thus, the use of the $Ru(CO)(Cl)_2(Ph_3P)_3$ starting material provides a more rapid method for synthesis of this ruthenium (0) complex with comparable yield.

2. Metathesis of $Ru(CO)(CH_3CN)(Ph_3P)_3$

Several attempts were made to react $Ru(CO)(CH_3CN)(Ph_3P)_3$

with the ligand, Ph_2MeP, to form $Ru(CO)(CH_3CN)(Ph_2MeP)_3$. This reaction was tried on a small as well as a large scale. On the small scale, an intractable yellow oil formed which could not be crystallized with a variety of solvent media. In an attempt to avoid this oil formation, a larger amount of starting material was metathesized. Although some crystals were obtained, they were found to be a mixture of partially substituted compounds and starting material. The methyl region of the ^1H nmr spectrum of this solid product exhibited complex splitting patterns suggesting that there was not just one complex present. From these results, it was concluded that this complex could not be made simply by metathesis of the zero valent triphenylphosphine complex. An electrochemical route would most likely be the best procedure using as a precursor $Ru(CO)(Cl)_2(Ph_2MeP)_3$. This complex can be electrolyzed at about -2.35 V in the presence of excess Ph_2MeP in acetonitrile at a mercury electrode.

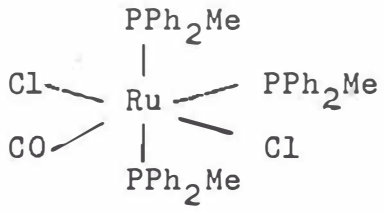
Using each of the ligands, Ph_2MeP and Et_3P, and the starting material $Ru(CO)(CH_3CN)(Ph_3P)_3$, the metathetical synthesis of $Ru(CO)(CH_3CN)(PhMe_2P)_3$ and $Ru(CO)(CH_3CN)(Et_3P)_3$ were attempted. In both reactions the reaction mixture changed from red-orange to yellow indicating reaction. However, the only product obtained in each case was an oil. Many different solvent media were used in trying to crystallize these oils but to no avail. Therefore, it was concluded that a metathetical route was not feasible and a better route might be potentiostatic reduction to make the desired ruthenium (0) compounds. An electrochemical approach

appears practical for the compound with the ligand $PhMe_2P$ where a suitable ruthenium (II) starting material, $Ru(CO)(Cl)_2(PhMe_2P)_3$, is available. The electrolysis can be carried out at a potential of about -2.50 V with a mercury cathode. In the case of the triethylphosphine ligand, the lack of a convenient route to the precursor, $Ru(CO)(Cl)_2(Et_3P)_3$ precludes synthesis of the desired product.

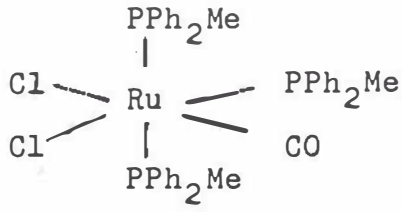
Summary and Conclusions

The ruthenium (II) complex, $Ru(CO)(Cl)_2(Ph_3P)_3$, was synthesized by reaction of $Ru(H)(Cl)(CO)(Ph_3P)_3$ with HCl and complete evaporation of the methylene chloride solvent. Dissolution of $Ru(CO)(Cl)_2(Ph_3P)_3$ in acetonitrile resulted in triphenylphosphine dissociation and formation of a dimer, $(Ru(CO)(Cl)_2(Ph_3P)_2)_2$ On the basis of its physical properties the isolated dimer appears to be an isomer of a similar dimer previously reported (1).

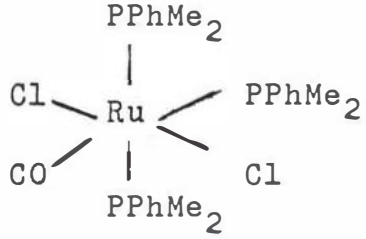
Metathesis of $Ru(CO)(Cl)_2(Ph_3P)_3$ in hexane with Ph_2MeP and $PhMe_2P$ led to the preparation of $Ru(CO)(Cl)_2(Ph_2MeP)_3$ and $Ru(CO)(Cl)_2(PhMe_2P)_3$, respectively. These compounds were characterized by infrared spectroscopy, ^1H and ^{31}P nmr spectroscopy, and elemental analysis. The following isomeric structures are in accord with the available data but distinction between the isomers is not possible.



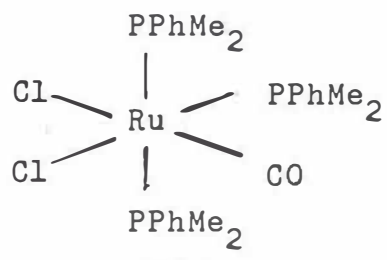
I-A



I-B



II-A



II-B

Metathesis of $Ru(CO)(Cl)_2(Ph_3P)_3$ with Et_3P yielded a mixture of the desired complex, $Ru(CO)(Cl)_2(Et_3P)_3$ and mixed triphenylphosphine/triethylphosphine complexes which could not be separated.

Electrochemical reduction of $Ru(CO)(CH_3CN)(Ph_3P)_3$ in acetonitrile with excess triphenylphosphine gave $Ru(CO)(CH_3CN)(Ph_3P)_3$ in good yield. This synthetic route is much more convenient and rapid than that based (1) on reduction of the dimer, $(Ru(CO)(Cl)_2(Ph_3P)_2)_2$ owing to the enhanced solubility of the starting material.

Metathetical reaction of $Ru(CO)(CH_3CN)(Ph_3P)_3$ with Ph_2MeP, $PhMe_2P$ or Et_3P in acetonitrile failed to yield ruthenium complexes of the type $Ru(CO)(CH_3CN)L_3$. In each case a mixture of products was obtained as intractable oils.

The redox properties of $Ru(CO)(Cl)_2(Ph_2MeP)_3$ and $Ru(CO)(Cl)_2(PhMe_2P)_3$ were determined in 0.100 M tetraethylammonium perchlorate acetonitrile solutions. Polarographic and voltammetric data indicate that these compounds are reduced in two irreversible two-electron steps. The two electroactive species are formed in solution through phosphine/solvent exchange. The limiting polarographic currents were kinetically controlled by this exchange reaction especially in the presence of excess ligand. The electroanalytical data suggest that these compounds may be electrochemically reduced to the corresponding ruthenium (0) species. The potentials for electrolysis of $Ru(CO)(Cl)_2(Ph_2MeP)_3$ and $Ru(CO)(Cl)_2(PhMe_2P)_3$ were determined to be -2.38 V and -2.53 V, respectively. A mercury cathode should be used for electrolysis.

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Vita

Name:	Joann Carol Bady
Place of Birth:	Chicago, Illinois
Year of Birth:	1956

Post Secondary
Education and Degrees:

North Central College
Naperville, Illinois
1974-1978
B.A. (Chemistry)

Eastern Illinois University
Charleston, Illinois
1978-1983
M.S. (Chemistry)